4. ANALYTICAL CHEMISTRY

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Procedures:

4. ANALYTICAL CHEMISTRY

4.1 OVERVIEW

During the past 40 years, EML has developed analytical procedures for the determination of specific gases, inorganic and organic constituents, and radionuclides. The procedures in this section are subdivided into two general categories: inorganics and radionuclides. All of the procedures have been written in a detailed manner to provide the user with sufficient information to obtain a quantitative result which is accurate, precise, free from chemical interference and contamination with specified detection capabilities. These procedures are currently not used at EML but they are still valid and are used at other laboratories.

The procedures described in the inorganic subsection have been applied to a variety of research programs. Most of the analyses for trace metals are performed by atomic absorption spectrometry and instrument operational conditions are provided. Anions are routinely determined by ion chromatography for various environmental matrices. Again, operational conditions, limitations and interferences are provided.

The second subsection is devoted to radionuclide measurements and radiochemical procedures. Information about background corrections, efficiency determination, and quality control methods and limits of detection are also included. The radiochemical procedures described are designed for various environmental matrices. The sample preparation portion introduces the procedure so that representative, homogeneous, and equilibrated samples are obtained. Next, separation and purification techniques are described to obtain a radiochemically pure sample. Measurement techniques, including limits of detection, quality control or special procedural precautions are also included.

4.3 INORGANICS

4.3.1 SCOPE

Described in this section are the inorganic procedures currently not in use at EML. These procedures have been adapted for inorganic constituent analyses in air filter extract, water, rain water, and certain soils and sediments. Atomic absorption spectrometry is used for determination of metals, ion chromatography for specific anions, and a specific ion electrode is used for fluoride determination. These procedures have been thoroughly tested; accuracy, precision, and lower limits of detection have been established. Effects from interferences and contamination are detailed in each appropriate procedure.

4.3.2 Elemental Analyses

Anions-01-E

ANIONS - ION CHROMATOGRAPHY

APPLICATION

This procedure has been applied to precipitation and lake water samples and the aqueous extracts of air filters. Anions are separated and quantitated using an ion chromatograph.

Ion chromatography (IC) is a form of high pressure liquid chromatography (HPLC) which utilizes an anion exchange column (separator column), a cation exchange column (suppressor column), and a conductivity detector to identify and quantitate anions in solution. Anions analyzed by IC include F^-, Cl^-, $HPO_4^=$, Br^-, NO_3^-, and $SO_4^=$. Detection of ng mL^{-1} anion concentrations is possible since the suppressor column converts the highly conductive eluent ($NaHCO_3/Na_2CO_3$) into a slightly conductive acid (H_2CO_3).

SPECIAL APPARATUS

1. Ion chromatograph - i.e., Dionex Corporation Model 2020 i (Dionex Corp., Sunnyvale, CA).

2. HPIC-AG4 anion guard column - No. 35210 (Dionex Corp., Sunnyvale, CA).

3. HPIC-AS4 anion separator column - No. 35311 (Dionex Corp., Sunnyvale, CA).

4. Anion fiber suppressor - No. 35350 (Dionex Corp., Sunnyvale, CA).

5. Strip chart recorder - available from chemical supply houses, i.e., Houston Omnigraphic-3000, 1 V input.

6. 10-mL plastic syringes - available from chemical supply houses, i.e., Becton-Dickinson No. 5604.

7. 50-mL disposable plastic beakers - Fisher No. 2-544-38 (Fisher Scientific, Fairlawn, NJ).

8. 100-µL Eppendorf pipette - available from chemical supply houses.

SPECIAL REAGENTS

1. 0.0027M $NaHCO_3$/0.0022M Na_2CO_3 eluent - weigh out 4.292 g $NaHCO_3$, and 4 413 g of Na_2CO_3. Combine and dissolve in 18.925 L (5 gallons) of deionized water.

2. 0.27M $NaHCO_3$/0.22M Na_2CO_3 concentrated eluent - weigh out 2.268 g $NaHCO_3$ and 2.332 g of Na_2CO_3. Combine and dissolve in 100 mL of deionized water.

3. 0.054M H_2SO_4 regenerant - dilute 14 mL of concentrated H_2SO_4 in 18.925 L (5 gallons) of deionized water.

4. Deionized water - water having a specific conductance of <2 µS cm^{-1} must be used to prepare all sample dilutions, eluents, and regenerants.

DETERMINATION

A schematic diagram of the ion chromatograph flow system is shown in Figure 1.

1. Prime the eluent and regenerant valves (see Dionex Operator's Manual, Chapter 2, Section 4.1).

2. Prime the pump (Dionex Operator's Manual, Chapter 2, Section 4.2).

3. Optimize the **Temperature Compensation Setting** for the eluent and columns used (Dionex Operator's Manual, Chapter 4, Section 4.4).

4. Connect the leads from the conductivity cell to the recorder. Adjust the recorder's zero and full scale settings using its **Zero** and **Calibration** knobs.

5. Select the analytical pump module's parameters:

   a. Choose the low and high pressure limits for each pump (Dionex Operator's Manual, Chapter 2, Section 4.3).

   b. Adjust the flow rate to 2 mL min^{-1}.

   c. Turn the eluent switch **On** and the **Local/Remote** switch to **Local**.

6. Select the advanced chromatography module's parameters:

   a. Set the **Load/Inject** switch to **Load**, the "A" valve to **Off**, the "B" valve to **Off**, and the **Local/Remote** switch to **Local**.

7. Select the conductivity detector module's parameters:

   a. Turn the cell **On**, the auto-offset **Off**, and the **Local/Remote** switch to **Local**.

8. To equilibrate the system:

   a. Select the 30 µS cm^{-1} **Output Range.** This setting will allow the baseline to be monitored on the recorder.

   b. Set the recorder chart speed at 0.5 cm min^{-1}.

   c. Pump the eluent through the separator column, suppressor column and conductivity cell for ~ 15 min.

   d. Turn the **Auto-Offset On**. Adjust the position of the recorder's pen to ~ 20% scale with the **Zero** knob of the recorder.

e. Select the 1 µS cm^{-1} **Output Range**. Monitor the baseline. When the baseline drifts <1 chart division in 5 min, the system has equilibrated sufficiently to begin the analysis of the samples. Change the **Output Range** setting to 10 µS cm^{-1}.

f. Choose several samples from the group of samples to be analyzed. Scan each sample for peak height and retention time according to the directions outlined beginning in Step 9.

9. Sample injection:

a. Draw 10 mL of sample into a 10-mL plastic syringe.

b. Transfer the 10 mL of sample into a 50-mL disposable plastic beaker.

c. Add 100 µL of concentrated eluent to the 10-mL sample.

d. Draw the sample/concentrated eluent solution into the syringe.

e. Attach the syringe to the injection port.

f. Flush the injection loop with at least 1 mL of sample.

g. Inject the solution by setting the **Load/Inject** switch to **Inject.** Simultaneously press the **Mark** switch on the conductivity detector module so that the recorder's pen marks the time of injection. A chromatogram for the injected solution is obtained on the recorder. A typical chromatogram is shown in Figure 2.

h. When the chromatogram is finished, set the **Load/Inject** switch to **Load.**

i. If the peak heights are shorter than 15 chart divisions, increase the sensitivity by a factor of 3; change the **Output Range** setting to 3 µS cm^{-1}. (Peak height is defined as the distance between the constructed baseline and the peak maximum.) Repeat Steps f and h.

j. If the peak heights are >80 chart divisions, decrease the sensitivity by a factor of 3 (change the **Output Range** setting to 30 µs cm^{-1}). Repeat Steps f and h.

k. Continue adjusting the **Output Range** setting and keep repeating Steps f and h until the sample's peak heights are between 15-80 chart divisions high. If it is necessary to use the 100, 300 or 1000 µS cm^{-1} setting to keep the recorder's pen on scale, dilute the sample so that its peak heights are within the recommended limits when the detector is set on the 3, 10 or 30 µS cm^{-1} setting.

l. Analyze each sample at least twice with the detector set at the **Output Range** setting determined in Steps g-k. If the peak heights differ by more than 5%, inject the sample a third time. Continue analyzing the sample until the relative standard deviation of the peak heights is within 5%.

10. Calibration procedure:

a. Prepare at least four standards whose peak heights bracket the peak heights of the anion samples to be analyzed.

b. Analyze these standards according to the procedures outlined in **Determination**, Steps 6-9.

c. Multiply the peak height measured by the **Output Range** selected for analysis. (The peak height values calculated in this manner are in units of µS cm^{-1}.)

d. Calculate the mean peak height for each anion.

e. Determine the retention time of each peak. (The retention time is the interval measured from the point of injection to the maximum point of the peak.)

f. Plot the average peak height value for each anion (y) versus its corresponding concentration value (x). The plot generated will be a straight line which can be described by the following function:

$$y = mx + b \quad (1)$$

where y is the peak height in μS cm^{-1}, m is the slope of the line, x is the anion concentration in μg mL^{-1} and b is the y intercept. The slope and intercept values will later be used to calculate the concentrations of anion samples.

g. Perform a linear regression analysis of the standard data. The correlation coefficient should be at least 0.99 or the calibration procedure should be repeated.

11. Determination of sample peak height and retention time:

a. Analyze each sample according to the procedure described in **Determination,** Step 9.

b. Identify the peaks by comparing their retention times with the retention times of the standards determined in **Determination**, Step 10.

c. Measure the height of each of the peaks in the chromatogram.

d. Calculate the mean peak height value from the duplicate measurements for each anion.

e. Calculate each sample's anion concentrations (x) using Equation (1), the average peak height value (y), the slope (m), and intercept values (b) determined in the **Determination**, Step 10.

LOWER LIMIT OF DETECTION (LLD)

The LLD is defined as the anion concentration which produces a detector response (peak height) that is twice the mean variation of the background (baseline noise).

The following LLDs were determined using a 50-µL injection loop and the columns, sensitivity, parameters, eluent, and regenerant listed in this section.

F^-	0.01 µg mL^{-1}
Cl^-	0.01 µg mL^{-1}
$HPO_4^=$	0.02 µg mL^{-1}
Br^-	0.02 µg mL^{-1}
NO_3^-	0.02 µg mL^{-1}
$SO_4^=$	0.02 µg mL^{-1}

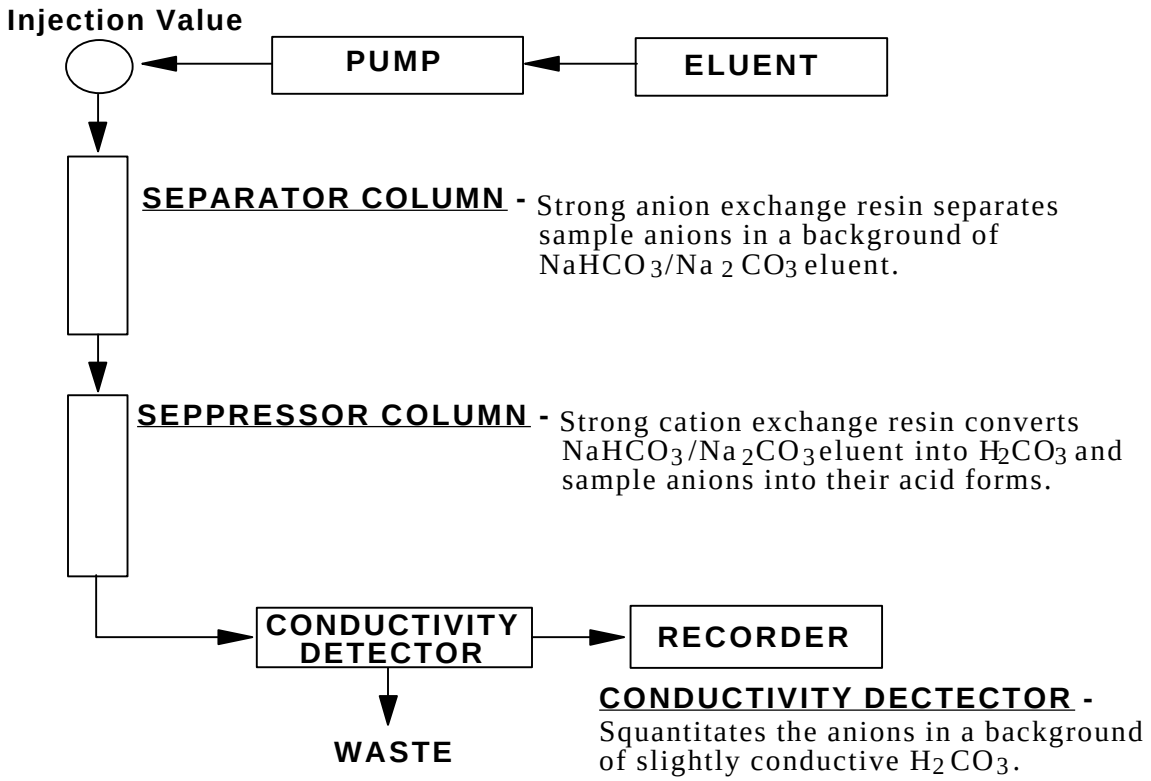

Figure 1. Schematic diagram of the ion chromatograph flow system.

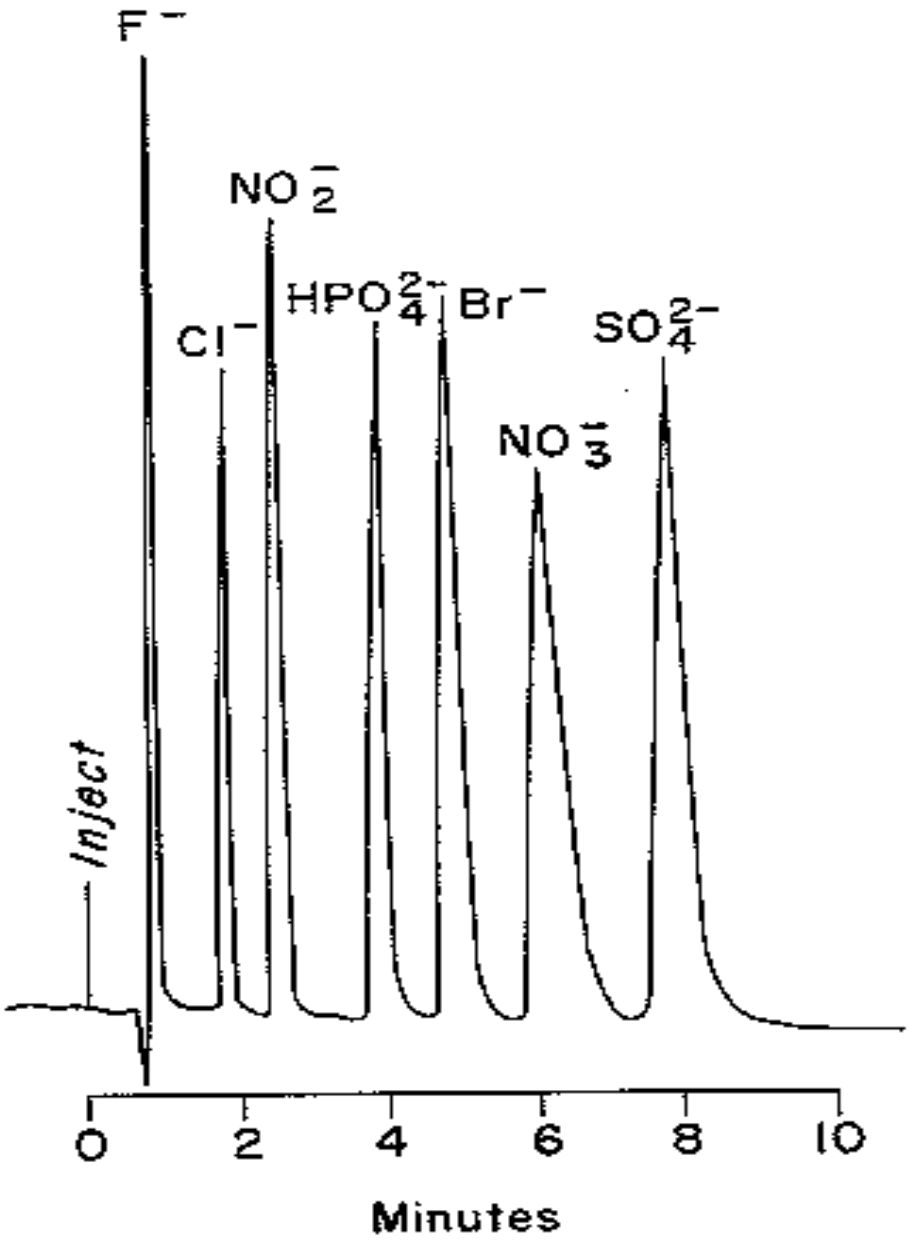

Figure 2. Typical ion chromatogram.

Ca-01-E

CALCIUM - ATOMIC ABSORPTION SPECTROMETRY

APPLICATION

Bone, milk, food, and vegetation ash have been analyzed by this procedure. Stable Ca is determined by atomic absorption (AA) spectrometry. The sample is dissolved in HCl. Lanthanum is added as a releasing agent to eliminate chemical interference of phosphorus, aluminum, silicon and sulfur and their anions in the analysis of Ca.

SPECIAL APPARATUS

1. Double beam AA spectrometer (e.g., Perkin-Elmer Model 603).

2. Boiling burner head recommended (Perkin-Elmer Corp., Norwalk, CT).

3. Recorder readout (optional).

4. Acetylene and filtered compressed air.

SPECIAL REAGENTS

1. Calcium "AA standard" stock solution - 1000 mg L^{-1} (Aztec Instruments, Inc., Westport, CT).

2. Stock La solution: 5% - dissolve 58.65 g of La_2O_3 (obtained from Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, IL) in 250 mL of HCl and dilute to 1 L with water.

3. Calcium standard solutions - prepare dilutions of the stock Ca solution to contain 0, 1, 2, 5, 8, and 10 mg L^{-1} Ca, all in 1% La and 1:19 HCl. If other concentrations of Ca are required, the final standard solutions should contain 1% La in 1:19 HCl.

4. Deionized or doubly-distilled water should be used for sample preparation and reagents.

SAMPLE PREPARATION

1. Prepare samples by ashing as in the radiochemical procedure for ^{90}Sr (see Section 4.5.4, Sr-02-RC, this volume).

2. Weigh 1 g of ash into a 100-mL beaker (0.1 g is adequate for bone ash). Add 1 mL of 1:1 HCl and evaporate to dryness. Repeat one time.

3. Dissolve the residue in 10 mL of 1:11 HCl and filter by gravity through a 7 cm Whatman No. 42 filter paper. Collect the filtrate in a 100-mL volumetric flask and wash the residue with hot water until the total volume is about 50-75 mL.

4. Cool to room temperature and dilute to volume with water.

5. Make a rough estimate of the concentration of Ca in the sample by making an absorption measurement on the instrument and comparing it with a Ca solution of known concentration.

6. Make the necessary dilution so that the final concentration of Ca is in the 1-10 mg L^{-1} range and the solution contains 1% La in 1:19 HCl.

DETERMINATION

1. Measure the Ca standard solutions and a blank with the AA spectrometer. (Detailed instructions are not given here as they apply only to a specific instrument.)

2. Measure the sample solutions. At least two different sample concentrations should be analyzed to determine any effect from matrix interferences.

3. Prepare a calibration curve by plotting absorbance versus concentration of the standard Ca solutions.

4. Read off the Ca concentration of the samples from the calibration curve.

5. Calculate the amount of Ca in the sample by correcting for Ca in the blank, dilutions and sample weight. The chemical yield is assumed to be 100%.

Ca-02-E

CALCIUM - PERMANGANATE TITRATION OF THE OXALATE

APPLICATION

This procedure is applicable for wet- or dry-ashed biological materials and for inorganic materials. In soil analyses, the Ca must be separated from interfering elements before determination.

Calcium oxalate is precipitated by excess ammonium oxalate from an ammonium acetate solution buffered to a pH of 4.5-5.0. The precipitate is dissolved in dilute H_2SO_4 and the liberated oxalic acid is determined by permanganate titration.

SPECIAL APPARATUS

1. 40-mL short cone, heavy walled, centrifuge tubes.

2. 5-mL buret - calibrated in 0.01-mL increments.

3. Stand to accommodate automatic volume dispensers.

4. Automatic volume dispensers - 1 mL, 3 mL, 4 mL, and 10 mL.

SPECIAL REAGENTS

1. Standard Ca solution - 2.000 mg Ca mL^{-1}. Dissolve 5.004 g oven-dried reagent grade

$CaCO_3$ in a 1-L volumetric flask by adding distilled water containing 12 mL of HNO_3 and diluting to volume. This amount of acid is sufficient to prevent precipitation of $Ca(OH)_2$. The solution is covered with a layer of toluene to prevent mold formation.

2. Saturated oxalic acid solution - 100 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) crystals per 600 mL of water.

3. Concentrated (stock solution) K permanganate solution - 6.900 g $KMnO_4$ L^{-1} H_2O.

4. Dilute K permanganate (for food, vegetation, and urine samples) - dilute one part of stock solution with nine parts of water. Dilute one part of stock solution with six parts of water (for milk and bone samples). Keep all permanganate solutions in the dark when not in use.

5. Methyl red indicator solution - dissolve 100 mg of the dye in 60 mL of 95% ethanol and dilute to about 100 mL with water.

6. Ammonia wash solution - 5-10 drops of NH_4OH L^{-1} of water.

SAMPLE PREPARATION

Biological samples are dry ashed at 550°C or wet ashed with concentrated HNO_3. In the latter procedures, hydrogen peroxide is added to obtain a white ash. Since the quantity of the elements that interfere is at a minimum in these samples, an aliquot of the final ash solution is used directly for Ca determination.

In the analysis of soil for Ca, it is preferable to prepare a separate sample for Ca analysis or to remove the aliquot immediately after dissolution of the soil. The Ca aliquot is purified using the radiochemical procedure for ^{90}Sr (see Section 4.5.4, Sr-02-RC, this volume), without adding Sr or Y carrier, and is processed through to the Ba precipitation step. The sample is then ready for Ca determination.

Since HCl interferes with the permanganate titration, it should not be used to dissolve samples or precipitates. Nitric acid should be used wherever possible.

DETERMINATION

1. Transfer the proper sized aliquot to a 40-mL conical heavy-walled centrifuge tube. (The aliquot should contain between 0.5 and 2 mg of Ca. This is the preferred range, however, it is possible to determine Ca from 0.1 to 10 mg.)

2. Add 4 mL of 1:4 acetic acid. Stir.

3. Add 3 mL of saturated oxalic acid. Stir.

4. Add 7-10 drops methyl red (see **Note 1**). Add 1:4 ammonium hydroxide drop by drop (see **Note 2**) until just alkaline to the methyl red, a yellow color.

5. Add 1:4 acetic acid drop by drop until faintly acid to the methyl red, an orange color. Let stand at room temperature overnight or in a water bath at 75°C for 3 h.

6. Centrifuge. Decant supernate and discard.

7. Wash precipitate with 10 mL of NH_3 wash solution, stirring precipitate and rinsing down the sides of the tube. Place in a hot water bath for 1 h.

8. Cool. Centrifuge. Decant and discard washings. Carefully place a tissue over the tube while in an inverted position and leave in a tube rack until dry.

9. Add 1 mL of 1:9 H_2SO_4. Heat in water bath to 70°-80°C until precipitate is completely dissolved (see **Note 3**).

10. Titrate with dilute permanganate solution to a faint pink shade that persists at least 30 sec. Rewarm during titration if necessary (see **Note 4**).

Notes:

1. If methyl red is added before the saturated oxalic acid, an interfering brown coloration may be produced.

2. If NH_4OH is added too rapidly, local concentrations may precipitate hydroxides.

3. Milk and bone samples usually require 2-4 mL of 1:9 H_2SO_4.

4. Chloride will interfere in the permanganate titration by reducing MnO_4 to MnO_2. Samples giving a brownish color during titration should be discarded.

CALIBRATION

One milliliter of the standard Ca solution containing 2 mg Ca is analyzed by the procedures given under **Determination**. The volume of permanganate solution that is needed is then equivalent to 2 mg Ca. At least two standard Ca determinations should be run with each set of unknowns on each day. A reagent blank will usually require less than one drop of permanganate and may usually be neglected unless very accurate results are required or the total Ca is < 0.1 mg.

COMPUTATION

1. Divide the volume of permanganate used to titrate the Ca standard by two to determine mL of titrant per mg Ca.

2. Divide the volume of permanganate required for the sample by the value obtained in Step 1 to determine mg of Ca per aliquot used.

3. Apply the proper dilution factor to determine the total Ca in the sample.

   Example: an unknown solution of 100-mL volume contains ~1 g of Ca (10 mg mL^{-1}). In the determination, 5 mL is diluted to 50 (Ca ~1 mg mL^{-1}) and 1 mL is taken for analysis.

   The standard requires 4.84 mL of permanganate for 2 mg of Ca, therefore, 2.42 mL of permanganate = 1 mg Ca.

The sample requires 2 mL, therefore, it contains

$$2.0/2.42 = 0.827 \text{ mg}$$

The dilution factor is 100/5 x 1 x 50 = 1000, therefore, the total Ca = 1000 x 0.827 = 0.827 g.

F-01-E

FLUORIDE IN SOIL AND SEDIMENT - SPECIFIC ION ELECTRODE MEASUREMENTS

APPLICATION

This procedure is applicable to soils and sediments in the range of 1-1000 µg of F^- g^{-1} of sample.

The sample is fused with sodium hydroxide, extracted with water, adjusted to pH 5, and measured for F^- by specific ion electrode.

SPECIAL APPARATUS

1. Fluoride, specific ion electrode, e.g., Orion Model 96-09 (available from chemical supply houses).

2. Digital pH/ion meter, e.g., Orion Model 901 (available from chemical supply houses).

3. Standard pH and reference electrodes.

4. 100-mL Teflon beakers.

5. Nickel crucibles (100 mL).

6. 90-mL polyethylene centrifuge tubes.

SPECIAL REAGENTS

1. Sodium hydroxide (17N) - dissolve 670 g of sodium hydroxide pellets in distilled water and dilute to 1 L.

2. Total ionic strength adjuster buffer - add 84 mL of concentrated HCl, 242 g of Tris (hydroxymethyl) amino acid, and 230 g of Na tartrate to 500 mL distilled water. Stir until all the reagents have been dissolved, cool to room temperature and dilute to 1 L with distilled water.

3. Stock F^- solution - dissolve 2.2 g of NaF in distilled water and dilute to 1 L. Store in a polyethylene container.

SAMPLE PREPARATION

1. Weigh the sample (0.5, 1 or 1.5 g of soil or sediment) and transfer to an oxidized nickel crucible. (**Note**: the crucible is oxidized by heating in air.)

2. Add 12 mL of 17N NaOH to the crucible for each gram of sample and tap gently to disperse the sample in the sodium hydroxide solution.

3. Place the sample under a drying lamp and dry thoroughly (usually overnight).

4. Place the sample in a cold muffle furnace. Slowly raise the temperature to 600°C and fuse for 30 min.

5. Cool to room temperature and add 10 mL of distilled water.

6. Heat the sample gently on a hot plate to dissolve the fusion cake.

7. Slowly add 16 mL of concentrated HCl for each gram of sample to dissolve the remainder of the fusion cake.

8. Transfer the sample to a 100-mL Teflon beaker. Wash the crucible with a minimum amount of distilled water and transfer the washings to the Teflon beaker.

9. Evaporate to about 40-mL volume. Place pH electrodes in the sample and slowly add concentrated HCl to adjust the pH to 8.5.

10. Allow the sample to stand for several hours and recheck the pH. Adjust to pH 8.5, if necessary.

11. Transfer the sample to a 90-mL polyethylene centrifuge tube.

12. Centrifuge for 10 min. Decant into a tared polyethylene bottle and adjust pH to 5 by the addition of concentrated HCl. Reweigh the bottle and record the net sample weight.

13. Transfer the precipitate remaining from Step 12 back to the 100-mL Teflon beaker with a minimum amount of distilled water. Repeat Steps 8-12. Decant the wash into a separate tared polyethylene bottle. Reweigh the bottle and record the wash solution weight.

14. Retain samples for measurement of F^-.

DETERMINATION

1. Prepare 0.01, 0.1, 10, and 100 µg mL^{-1} F^- standards by serial dilution.

2. Combine 25 mL of the standard and 25 mL of total ionic strength adjuster buffer in a 100-mL plastic beaker. Add a small magnetic stirring bar.

3. Immerse the electrode at least 2 cm into the solution. Wait for the response to stabilize (~ 45-60 sec), mixing continuously using the magnetic stirrer.

4. Prepare a calibration curve plotting mV readings versus concentration of F^- on semilog graph paper. (The curve should be linear with a slope of 59 ± 2 mV.)

5. To analyze the samples, combine 25 mL of sample and 25 mL of the buffer in a 100-mL plastic beaker. Add a magnetic stirring bar. While stirring, add sequentially: 50-µL additions (using a µL dispensing pipette) of distilled water; 10,100, and 1000 µg mL^{-1} of F^- standards corresponding to 0, 0.1, 1 and 10 µg mL^{-1} of F^- additions. Record the mV response after each addition.

6. Plot the mV response versus added concentration of F^- on semilog graph paper. (The intersection of the curve with the concentration axis corresponds to the concentration of F^- in the diluted sample.)

7. Measure the sample and wash separately using the F^- ion selective electrode.

8. Compute the concentration of F^- in µg g^{-1} of sample by correcting for dilution and for the sample volume. Correct these values for reagent blanks processed in the same manner.

Notes:

1. Fluoride standard solutions may be prepared in a glass vessel, but must be analyzed within 4 h or transferred to polyethylene bottles for storage.

2. The total ion strength adjuster buffer must be prepared fresh every 4 weeks, and should be stored in a refrigerator.

3. The pH of the sample prior to analysis must be buffered to a pH of 5.5 to minimize the interference of $(OH)^-$ ion. Interference with the electrode response occurs when the concentration of $(OH)^-$ is greater than one-tenth the concentration of F^-.

4. The technique "Method of Additions" (see Step 5, **Determination**) is used to eliminate the effects of sample size and possible matrix problems.

LOWER LIMIT OF DETECTION (LLD)

The LLD of this procedure is estimated to be about 5 µg g^{-1} of the sample.

Hg-01-E

MERCURY - ATOMIC ABSORPTION SPECTROMETRY

APPLICATION

This procedure has been tested with NIST standard reference materials - coal, orchard leaves, and bovine liver - with sample sizes up to 1 g. The combustion procedure gives the total - inorganic plus organic - Hg and has been applied to dried samples of foods, water, urine, and biota.

The volatility of Hg and its compounds is utilized for separation. The sample is combusted in an atmosphere of O_2 and the Hg is collected in a liquid N_2 trap (Rook et al., 1972). The isolated Hg is measured by cold-vapor flameless atomic absorption (AA) spectrometry (Hatch and Ott, 1968).

SPECIAL APPARATUS

1. Double beam AA spectrometer, e.g., Perkin-Elmer Model 403 with strip chart recorder.

2. Combustion tube - heavy-walled quartz, ~ 2.0 cm ID x 45.0 cm long, with 19/38 female joint.

3. Condenser - standard wall, quartz, 1.3 cm ID x 20.0 cm long with 19/38 male joint.

4. Liquid N_2 trap - The liquid N_2 trap is prepared from a 0.95-L polyethylene aspirator bottle with an outlet tube near the bottom to drain off the liquid N_2. Two holes are cut 3.8 cm from the bottom so that the condenser tube can pass through. In use, the

bottle is filled with liquid N_2 to the top. The trap can be conveniently insulated with material from a styrofoam acid case. When the liquid N_2 is added, the contraction of the polyethylene forms a permanent seal around the condenser.

5. Oxygen-methane hand torch with high temperature fishtail tip.

6. Quartz wool.

7. One-way gas flow valve.

8. Glazed ceramic combustion boat.

9. Reduction cell (see Figure 1).

10. Magnetic stirrer.

11. Drying tube, 2.0 cm ID x 10.0 cm long, filled with silica gel.

12. Absorption cell, 1.0 cm ID x 15.0 cm long with quartz window.

SPECIAL REAGENTS

1. 10% $SnCl_2$ - dissolve 10 g $SnCl_2$ in 1:11 HCl and make up to ~ 100 mL.

2. 0.1N HCl solution.

3. Mercury "AA standard" stock solution, 1000 mg L^{-1}, Fisher Scientific Co., Fairlawn, NJ. Prepare a working standard of 100 ng mL^{-1}, as required, by dilution with water.

4. Liquid N_2.

5. Compressed gases: Ar, O_2, methane.

SAMPLE PREPARATION

1. Weigh up to 1 g of dried sample into a glazed ceramic combustion boat.

2. Assemble the combustion train shown in Figure 2.

3. Open the train at the junction of the combustion tube and condenser. Place an ~ 1.3 cm plug of quartz wool at the O_2 inlet port of the combustion tube.

4. Place the combustion boat with sample 2.5-5.0 cm from the quartz wool.

5. Place a 7.5-10.0 cm plug of quartz wool 12.5-17.0 cm away from the combustion boat.

6. Reconnect the combustion tube to the condenser.

7. Fill the liquid N_2 trap to the top.

8. Adjust the O_2 flow rate to 30 cm^3 min^{-1} and allow O_2 to flow through the combustion train.

9. With the O_2-methane torch fitted with a fishtail tip, heat downstream from the 10.0 cm quartz wool plug to red heat (~ 700°C).

10. Place a sheet of Siltemp on top of the combustion tube to maximize heating in the region. This region is where all pyrolysis products must be completely oxidized. (**Note**: Traces of incomplete pyrolysis products will cause extremely low recoveries of Hg, on the order of 0-10%. These products can be recognized as a yellow to brown color in the condenser or a distinct odor when the train is opened.)

11. Begin heating the sample slowly with a Meker burner starting near the O_2 inlet. Rapid oxidation must be avoided. Too rapid combustion is indicated by a red glow in the downstream quartz wool. Carefully remove moisture, carbonize, and finally ash the entire sample with the Meker burner.

12. With the O_2-methane torch, starting at the O_2 inlet, flame the entire combustion tube for 10 min.

13. Cool the combustion train for 15-30 min, then remove the liquid N_2 from the trap by draining through the outlet at the base of the polyethylene bottle.

CALIBRATION OF THE SPECTROMETER

The following instructions relate specifically to the spectrometer used here.

1. Optimize the response for Hg at a wavelength of 253.6 µM on the AA spectrometer.

2. Set the noise suppression at 2 and the scale expansion at 3.

3. Place the reduction cell on a magnetic stirrer and connect the inlet to an Ar gas cylinder. Connect the outlet to a drying tube containing Drierite which is connected in turn to the absorption cell.

4. Add 5 mL of 0.1N HCl to the reduction cell and flush the system with Ar at a flow rate of 2 L min^{-1}.

5. Turn the stopcocks of the reduction cell to bypass the cell.

6. Transfer 50 µL of a freshly prepared 100 ng Hg standard to the reduction cell.

7. Add 50 µL of 10% $SnCl_2$ to the reduction cell and stir for 2 min.

8. Turn both stopcocks simultaneously to pass Ar through the reduction cell. Record the percent absorption of the standard.

9. Remove the reduction cell and wash several times with 0.1N HCl and finally with deionized water. Discard the washings.

10. Repeat Steps 6-9 with 100, 200, and 250 µL of the 100 ng Hg standard.

11. Determine blanks before and after Hg standards are measured.

12. Subtract the mean blank value from the measured values and construct the calibration curve by plotting absorbance versus concentration.

DETERMINATION

1. Separate the combustion tube from the condenser. Wash the Hg from the condenser with one 3-mL and one 2-mL volume of 0.1N HCl, and transfer the washings to the reduction cell.

2. Add 50 µL of 10% $SnCl_2$ and stir for 2 min.

3. Turn both stopcocks simultaneously to pass Ar gas through the reduction cell. Record the percent absorption of the sample.

4. Subtract the blank value and read off the Hg concentration from the calibration curve.

LOWER LIMIT OF DETECTION (LLD)

The LLD for this procedure is estimated to be about 0.5 ng Hg.

REFERENCES

Hatch, W. R. and W. L. Ott
Anal. Chem., 40, 2085-87 (1968)

Rook, H. L., T. E. Gillis and P. D. LaFleur
Anal. Chem., 44, 1114-17 (1972)

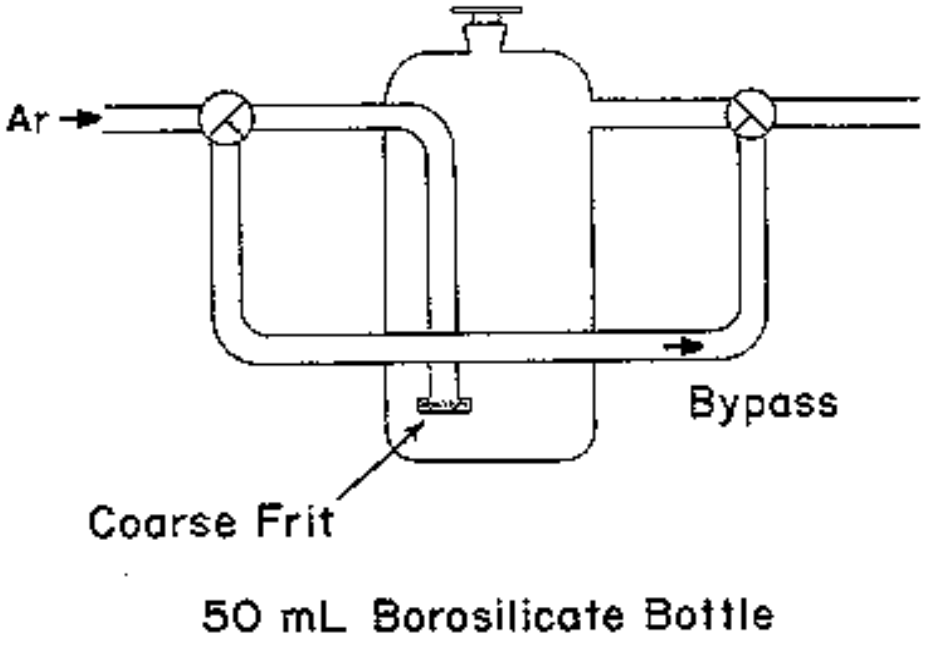

Figure 1. Reduction cell.

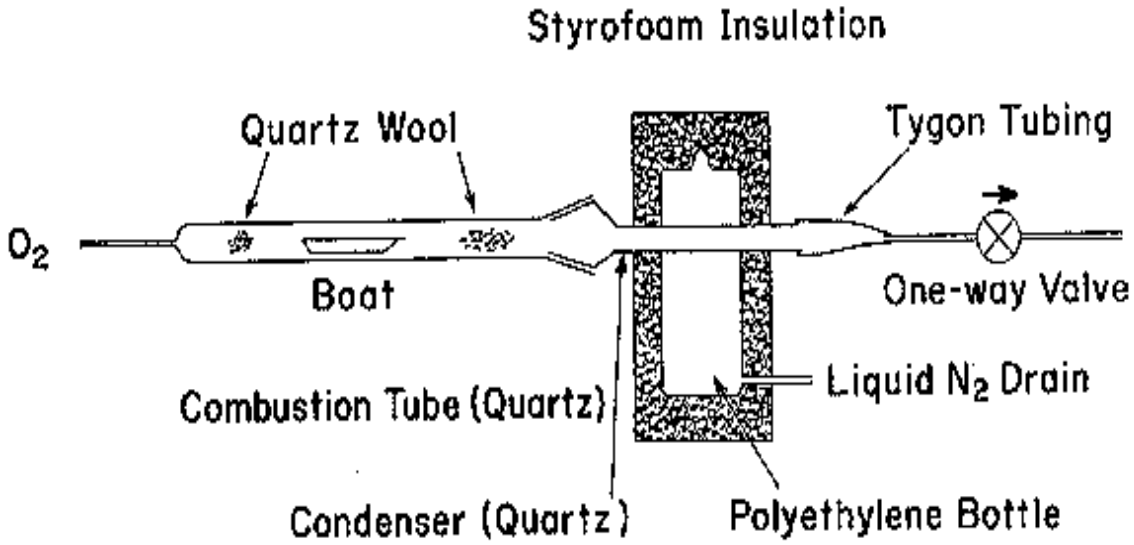

Figure 2. Combustion train for Hg determination.

NH_3^--01-E

AMMONIUM IN WATER AND PRECIPITATION SAMPLES - AUTOCOLORIMETRY

APPLICATION

This procedure has been applied to the analysis of NH_4^+ in water and precipitation samples.

Ammonium ions are determined spectrometrically at 630 nm. Alkaline phenol and hypochlorite react with NH_4^+ to form indophenol blue which is directly proportional to the NH_4^+ concentration. The blue color formed is intensified by the addition of sodium nitroprusside. Calcium and magnesium ions are interferences but may be eliminated by the addition of sodium citrate.

SPECIAL APPARATUS

Spectrometer [commercially available, e.g., Spectronic 21/MV].

SPECIAL REAGENTS

1. Phenol reagent - dissolve 76 g of phenol and 400 mg of disodium nitroprusside in water and dilute to 1 L. Store the reagent solution in a brown glass bottle.

2. Sodium citrate - dissolve 240 g of trisodium citrate dihydrate in 500 mL of water. Add 20 mL of 0.5M NaOH and gently evaporate the solution to <500 mL. Cool and dilute to 500 mL.

3. Sodium hypochlorite - commercial bleach, 5.25% active sodium hypochlorite.

4. Ammonium standard solution, 100 mg mL^{-1} - dissolve 4.4373 g of NH_4NO_3 in 1 L of H_2O.

SAMPLE PREPARATION

1. Add 47 mL each of the sample, reagent blank and dilutions of NH_4^+ standard solutions to individual 50-mL volumetric flasks.

2. Pipette 1 mL of sodium citrate into each flask and mix gently.

3. Pipette 1 mL of phenol reagent into each flask and mix gently.

4. Pipette 1 mL of sodium hypochlorite into each flask, mix thoroughly and store the samples in the dark for 3 h for color development.

DETERMINATION

1. Adjust the spectrometer operating conditions as predetermined for optimum sensitivity.

2. Use 1-cm path length cells for NH_4^+ concentrations >1 µg mL^{-1} and 10-cm path length cells for concentrations <1 µg mL^{-1}.

3. Measure the absorbancies for the sample, reagent blank, and NH_4^+ standard solutions at 630 nm.

DATA PROCESSING

1. Subtract the reagent blank absorbance reading from the sample and NH_4^+ standard readings.

2. Prepare a calibration curve using the NH_4^+ standard results. Determine the sample concentration from the calibration curve.

LOWER LIMIT OF DETECTION (LLD)

The LLD for this procedure is estimated to be 10 ng mL^{-1}.

Sr-01-E

STRONTIUM - ATOMIC ABSORPTION SPECTROMETRY

APPLICATION

Bone, milk, fresh water, food, vegetation, and excreta have been analyzed by this technique.

Stable Sr is determined by atomic absorption (AA) spectrometry. The sample ash is dissolved in HCl and La is added to reduce interferences from phosphate, silicate, and aluminate that occur in the flame. A preliminary measurement is made to obtain the range, and the final sample dilution is measured against standard solutions of similar chemical composition.

SPECIAL APPARATUS

1. Double beam AA spectrometer (e.g., Perkin-Elmer Model 603).

2. Acetylene and filtered compressed air.

SPECIAL REAGENTS

1. Strontium "AA standard" stock solution - 1000 mg L^{-1} (Aztec Instruments, Inc., Westport, CT 06880).

2. Stock La solution, 5% [the La_2O_3 was obtained from Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, IL 60185] - dissolve 58.65 g of La_2O_3 in 250 mL of HCl and dilute to 1 L with water.

3. Strontium standard solutions - prepare dilutions of the stock Sr solution to contain 0.2, 0.4, 0.6, 0.8, and 1.0 mg L^{-1} of Sr all in 1% La and 1:19 HCl solution. If other concentrations of Sr are required, the final standard solutions should contain 1% La in 1:19 HCl.

4. Deionized or doubly-distilled water should be used throughout for sample preparation and reagents.

SAMPLE PREPARATION

1. Prepare samples by ashing as in the radiochemical procedure for ^{90}Sr (see Sr-02-RC).

2. Weigh 1 g of ash into a 100-mL beaker. Add 5 mL of 1:1 HCl and evaporate to dryness. Repeat.

3. Dissolve the residue in 2 mL of 1:9 HCl and filter by gravity through a 7 cm Whatman No. 41 filter paper. Collect the filtrate in a 25-mL volumetric flask, wash the residue with water and dilute to volume with water.

4. Make a rough estimate of the concentration of Sr in the sample by making an absorption measurement on the instrument and comparing it with a solution of known Sr concentration.

5. Make the necessary dilution so that the final concentration of Sr is in the 0.1-1.0 mg L^{-1} range and the solution contains 1% La in 1:19 HCl. (**Note**: The final sample phosphate concentration should be < 300 mg L^{-1}.)

DETERMINATION

1. Measure the Sr standard solutions and a blank with the AA spectrometer. (Detailed instructions are not given here as they apply only to a specific instrument.)

2. Measure the sample solutions. At least two different sample concentrations should be analyzed to determine any effect from matrix interferences.

3. Prepare a calibration curve by plotting absorbance versus concentration of the standard Sr solutions.

4. Read off the Sr concentration of the samples from the calibration curve.

5. Calculate the amount of Sr in the sample by correcting for Sr in the blank, dilutions and sample weight. The chemical yield is assumed to be 100%.

LOWER LIMIT OF DETECTION (LLD)

The LLD for this procedure is estimated to be about 20 µg L^{-1}.

U-01-E

URANIUM IN URINE - FLUORIMETRY

APPLICATION

The procedure was developed for urine specimens; however, it may be used for other materials after the U has been sufficiently isolated from the matrix.

Uranium is determined from the fluorescence produced when fused with NaF and exposed to ultraviolet light. The fluorimeter will measure from 1-10,000 μg of U L^{-1} of urine.

SPECIAL APPARATUS

1. A 5-mL hypodermic syringe connected by plastic tubing to an 0.5-mL Mohr (graduated in 0.01 mL) pipette which is mounted o a ring stand.

2. Platinum fluorimeter dishes fabricated from 0.004-cm thick, 2.5-cm diameter blanks. A circular depression 1.3-cm in diameter and 0.4-cm deep is formed at the center.

3. A booster pump with a pressure regulator, set for 45 cm (Hg), is required for natural gas supply to obtain fusion temperatures within 25-30 sec.

4. Uranium fluorimeter (Giovanni et al., 1954).

5. A pellet dispenser made by cutting a 1-mL glass hypodermic syringe to leave the full bore open. The plunger is fitted with a stop so that the maximum opening will contain 100 ± 10 mg of NaF.

6. Platinum loop dish holders made of 2-mm platinum rod, mounted on a ring stand so that the dishes are held in the zone of maximum flame temperature.

7. Low temperature hot plate covered with 0.6-cm transite. The transite has three rows of 1.3-cm circular cutouts for holding dishes for evaporation.

8. Transite racks to hold nine sample dishes are fitted with legs for stacking.

SPECIAL REAGENTS

1. Reagent grade NaF - several lots from different manufacturers should be tested to obtain material with a minimum blank reading and high U sensitivity. Sufficient reagent from the best lot should be obtained to last for several years.

2. Stock solution "A" (500 µg mL^{-1}) - dissolve 58.9 mg of pure of U_3O_8 in 2 mL of HNO_3 and evaporate to dryness. Take up with water containing 10 drops of HNO_3, transfer to a 100-mL Pyrex volumetric flask and dilute to volume.

3. Standard solution "B" (50 µg mL^{-1}) - transfer 10 mL of solution "A" to a 100-mL Pyrex volumetric flask. Add 10 drops of HNO_3 and dilute to volume.

4. Standard solution "C" (5 µg mL^{-1}) - transfer 1 mL of solution "A" to a 50-mL Pyrex volumetric flask, add five drops of HNO_3 and dilute to volume.

Note:

It is important that the standard solutions be slightly acid to prevent hydrolysis and absorption of U. They should be stored in polyethylene bottles.

SAMPLE PREPARATION

Properly preserved urine samples are analyzed as received. Samples that are cloudy are treated with 1% by volume of HCl and allowed to stand overnight before analysis.

Those that do not become clear are wet ashed with HNO_3 and 30% H_2O_2 and made up to the original volume with water.

The addition of about 1% by volume of HCl at the time of sampling will prevent deterioration.

INSTRUMENT STANDARDIZATION

Prior to initial use, allow the fluorimeter to warm up for 15 min. A permanent glass standard is used for daily adjustment of the instrument and for stability checks after reading each sample. A 0.6 µg U standard is adjusted to 6000 divisions and the prepared glass standard is read. This reading is recorded and in subsequent use of the instrument the meter is set at this value by adjusting the phototube voltage. The glass standard prepared at EML is equivalent to 0.27 µg of U and given an instrument response of 2700 divisions.

DETERMINATION

A. Measurement.

1. Analyze all samples in triplicate.

2. Rinse pipette with water and the sample before taking the aliquots.

3. Pipette 0.1 mL of urine onto each of three platinum dishes.

4. Evaporate to dryness on the low heat hot plate.

5. Ignite the residue over a Meker burner.

6. Cool and add 100 ± 10 mg of NaF.

7. Fuse completely over a Meker burner with gas at 45-cm Hg. The temperature of the flame should be such that complete fusion takes place within 25-30 sec.

8. Cool by holding dish in air, with platinum tipped forceps, for a few seconds. Place in a transite rack to cool completely.

9. Read the fluorescence of each sample.

10. Calculate the U from a calibration factor or calibration curve.

B. Cleaning platinum dishes.

Dishes are cleaned daily since there are sufficient platinum dishes available for a full day of analyses. Samples that read >50 divisions are separated from those that read <50 divisions for special cleaning. After the sample have been read, remove the bead by washing with hot water. The low reading dishes are allowed to stand in hot 1:1 HNO_3 for at least 15 min and preferable overnight. The high reading dishes are fused with a small amount of $K_2S_2O_7$ (potassium pyrosulfate), washed in tap water and then placed in 1:1 HNO_3 as above.

When ready to use the dishes, rinse with tap water, then distilled water and dry over a flame. Select three dishes at random and run blank determinations. If one or more show a reading above a normal blank, reclean the entries batch.

C. Standardization.

The quantity of U in the samples is determined from a calibration curve. The standards are prepared by pipetting suitable portions of standard U solutions onto platinum dishes and treating as described in **Determination**. A new calibration is run each time a fresh bottle of NaF is put into use. For calibration, four standards are used in each instrument range. The dilutions are always made fresh from solutions A, B, and C described above. The median net meter readings from triplicate aliquots are plotted against the quantity of U to give the calibration curve or the slope of the straight line obtained is used as calibration factor for sample analyses.

Background fluorescence reduces the accuracy of the analysis at very low concentrations (1-10 µg L^{-1}). High concentrations (over 1000 µg) are usually diluted prior to analysis to prevent saturation of the fluorescence in the bead.

DATA PROCESSING

The net median value of the triplicate results is used to determine the micro grams of U in the sample. The U values corresponding to the meter reading are calculated using the standardization factors for the instrument (see **Note** 4).

The following equation is used for calculating the $\mu g\ L^{-1}$.

$$(DR - B)\ F = \mu g\ L^{-1}$$

where

D = the meter deflection of the sample,
R = the meter range (1, 10, or 100),
B = the meter deflection of the blank (always on the 1 scale), and
F = the factor in $\mu g\ U\ L^{-1}$ per unit deflection for the meter range used.

Since the fluorimeter is set to a fixed value for the glass standard (27 on the 100 scale for 2700 $\mu g\ U\ L^{-1}$), F is normally unity. This may vary slightly from time to time on the 1 and 10 scales.

Notes:

1. The NaF should not be allowed to stand open to the air since it is hygroscopic.

2. Tongs should not be used to hold the dishes in the flame as the flux tends to run toward the cold spot. Using the loop, a uniform bead confined to the depression will be produced.

3. After fusion, allow the dish to cool for at least 10 min and not more than 30 min before reading.

4. The whole problem of quenching is one that has not been satisfactorily explained or investigated particularly at extremely low levels of U concentration. It is known that colored ions will produce quenching, but the degree must be determined for each

sample. Experimentally, there appears to be no quenching of U fluorescence in urine samples and quenching in general is minimized when pure NaF flux is used, rather than mixtures.

REFERENCE

Giovanni, H. J. D., R. T. Graveson, and B. Dwork
"Photofluorimeters for Determination of Uranium and Be Concentration"
New York Operations Office Report NYO-4508, U. S. Atomic Energy Commission (1954)

4.3.3 Multielemental Analyses

M-01

CADMIUM AND LEAD IN HUMAN EXCRETA AND COMPOSITE DIET SAMPLES - ATOMIC ABSORPTION SPECTROMETRY

APPLICATION

This procedure is applicable to biological matrices such as: composite diet and excreta samples and also, orchard leaves, bovine liver, pine needles, tomato leaves, spinach, and fish homogenate.

The samples are wet ashed using high purity HNO_3 or are dry ashed. Cadmium and Pb are determined by graphite furnace atomic absorption (AA) spectrometry without extraction or matrix modification.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin-Elmer Model 603 equipped with a 2100 heated graphite atomizer (HGA), a deuterium-arc background corrector and a strip chart recorder.

2. Sub-boiling quartz distillation apparatus - Quartz & Silice Societe, Rue D'Anjou, Paris (Quartz Products Corp., Plainfield, NJ).

3. This procedure was developed and performed in a positive pressure laminar air flow clean room laboratory.

SPECIAL REAGENTS

1. High purity mineral acids - "Suprapur", EM Laboratories, Inc.

2. Commercially available Cd and Pb AA standards, 1000 µg mL^{-1} diluted to appropriate concentrations in the presence 32% HNO_3, i.e., Spex Industries, Inc.

SAMPLE PREPARATION

A. General.

1. All glassware and polyethylene containers are cleaned before use as follows: soak in 2% tetrasodium ethylene-diamine tetra-acetate solution for 12 h, thoroughly rinse with tap water, soak in 1:1 reagent grade HNO_3 for 12 h, rinse at least three times with demineralized water then air dry.

2. Approximately 10% of the total samples prepared should be reagent blank samples which contain equivalent amounts of the reagents used in the preparation procedure.

B. Urine (wet ashing).

1. Transfer 25 mL of concentrated HNO_3 into a 1000-mL heavy walled Pyrex beaker.

2. **Slowly**, add a 750-mL aliquot of a 2-L urine sample into the beaker (see **Note 1**). **Caution** - sample may effervesce or froth over beaker if acid is added to urine.

3. Evaporate the aliquot on a hot plate at a low heat until the entire sample is added to the beaker and the volume is reduced to ~ 100-150 mL.

4. Add 25 mL of concentrated HNO_3 to the sample, cover with a watch glass, and digest on low heat; evaporate the sample to dryness.

5. Repeat Step 4 until the residue is completely white.

6. Dissolve the sample residue with 12.5 mL of concentrated HNO_3 and 150-200 mL deionized-distilled water. Heat to boiling on medium heat. Cool to room temperature.

7. Transfer the sample to a 250-mL volumetric flask, dilute to volume and mix. Discard the residue.

8. Store the sample in a polyethylene container.

9. Measure the sample for Cd and Pb by graphite furnace AA spectrometry (see **Determination**).

C. Composite diet and feces (dry ashing).

1. Transfer a 250-g sample into a 400-mL heavy walled Pyrex beaker (see **Note 1**).

2. Place sample in a drying oven at 110°C until completely dry, ~ 24 h.

3. Place sample in a cold muffle furnace, slowly increase the temperature from 100-430 ± 20°C (do not exceed 450°C). Ash at 430°C for 24-60 h. Cool to room temperature.

4. Moisten the ash with deionized-distilled water and 5 mL of concentrated HNO_3. Dry the residue on a low heat.

5. Place the sample in a cold muffle furnace, slowly increase the temperature to 430°C and maintain for 12 h. Cool to room temperature.

6. Dissolve the sample with 12.5 mL of concentrated HNO_3 and 150-200 mL deionized-distilled water. Heat to boiling for 10 min. Cool to room temperature.

7. If a residue is present, filter the sample through a Whatman No. 42 filter paper, which has been previously washed with 5% HNO_3 and deionized-distilled water. Collect the filtrate in a 250-mL volumetric flask, dilute to volume and mix. Discard the residue.

8. Store the sample in a polyethylene container.

9. Measure the sample for Cd and Pb by graphite furnace AA spectrometry (see **Determination**).

D. Other biological materials (dry ashing).

The above dry ashing procedure is applicable to the other biological samples. Use desired amounts and proceed as described in Steps 1-9 above.

DETERMINATION

1. Prepare the AA spectrometer for graphite furnace analyses.

2. The Perkin-Elmer 603 AA spectrometer and the HGA 2100 graphite furnace instrumental parameters are as follows:

Element	Cd	Pb
Light source	Hollow Cathode Lamp	Hollow Cathode Lamp
Lamp current, mA	6	10
Wavelength, nm	228.8	283.3 217.0*
Slit setting, nm	0.7	0.7
D_2 background corrector	yes	yes
Graphite tube	uncoated	uncoated
Purge gas/flow	Ar/7.5 mL min^{-1}	Ar/7.5 mL min^{-1}
Gas flow mode	interrupt	interrupt
Dry	100°C/50-100 sec	100°C/50-100 sec
Char	250°C/20 sec	250°C/20 sec
Atomize	2100°C/5 sec	2220°C/5 sec
Working standard range	5-25 pg	100-500 pg 50-250 pg*
Standard and sample aliquot	25-50 µL	25-50 µL

***Most sensitive Pb wavelength.**

3. Dilute the sample solutions such that the Cd or Pb concentrations are within the standard ranges given above. Typical starting dilutions are as follows:

	Cd	Pb
Urine	(1/50)	(1/50)
Diet	(1/50)	(1/50)
Feces	(1/100)	(1/200)

4. Measure the nonspecific absorption of the sample dilutions in the background only (bkgd) mode on the AA spectrometer to ensure that the manufacturer's recommended maximum background absorbance is not exceeded.

5. Determine the Cd and Pb concentrations directly on the AA spectrometer, except for Pb in urine (see Step 6 below). The following steps apply to each trace metal:

   a. Measure the prepared standards in the AA/bkgd mode and establish the linear response range for Cd or Pb. A minimum of three readings is made for each standard or sample.

   b. Enter the concentration value for the highest standard from the linear response found in Step a into the S-1 concentration mode on the spectrometer.

   c. Set the mean absorbance obtained for this standard as the calibrating standard, S-1. The instrument is now calibrated for direct concentration readings.

   d. Use the other prepared standards and any available reference standards to check for the accuracy of the calibration.

   e. Measure the same size aliquots of the diluted samples as for the standards and the prepared blank samples to obtain direct Cd and Pb concentrations under optimum conditions.

   f. Check the calibration periodically using the prepared standards; if necessary, recalibrate as described in Step c.

   g. Calculate the Cd and Pb concentrations in the original sample by correcting for any blank contributions then multiplying by the appropriate dilution factors.

6. Determine the concentration of Pb in urine by the method of standard additions (see **Note 2**):

   a. Take three aliquots of the sample solution. Dilute one as described in Step 3 above. To the second and third aliquots, respectively, add a known quantity of Pb equivalent to once and twice the absorbance values found for the diluted sample alone. (The absorbance responses for the sample plus the additions must be linear.)

b. Measure each solution and obtain mean absorbances.

c. Plot these absorbance readings against the added concentrations.

d. Extrapolate the resulting straight line through zero absorbance (see Figure 1).

e. Obtain the Pb concentration in the diluted sample from the intercept on the concentration axis.

f. The prepared blank samples are measured as described in Step 5 above.

g. Calculate the Pb concentration in the original sample by correcting for any blank contributions then multiplying by the appropriate dilution factors.

Notes:

1. Smaller amounts of diet and human excreta may be used for the determination of Cd and Pb by graphite furnace AA. This procedure was developed for large sample sizes to accommodate aliquoting for several other investigations of the same sample.

2. The method of standard additions is required to compensate for the matrix interferences observed for the direct determination of Pb in urine. Figure 1 illustrates the Pb suppression effects found for several urine samples.

LOWER LIMIT OF DETECTION (LLD)

The LLD for this procedure is estimated to be about 10 µg L^{-1} for Cd and 20 µg L^{-1} for Pb.

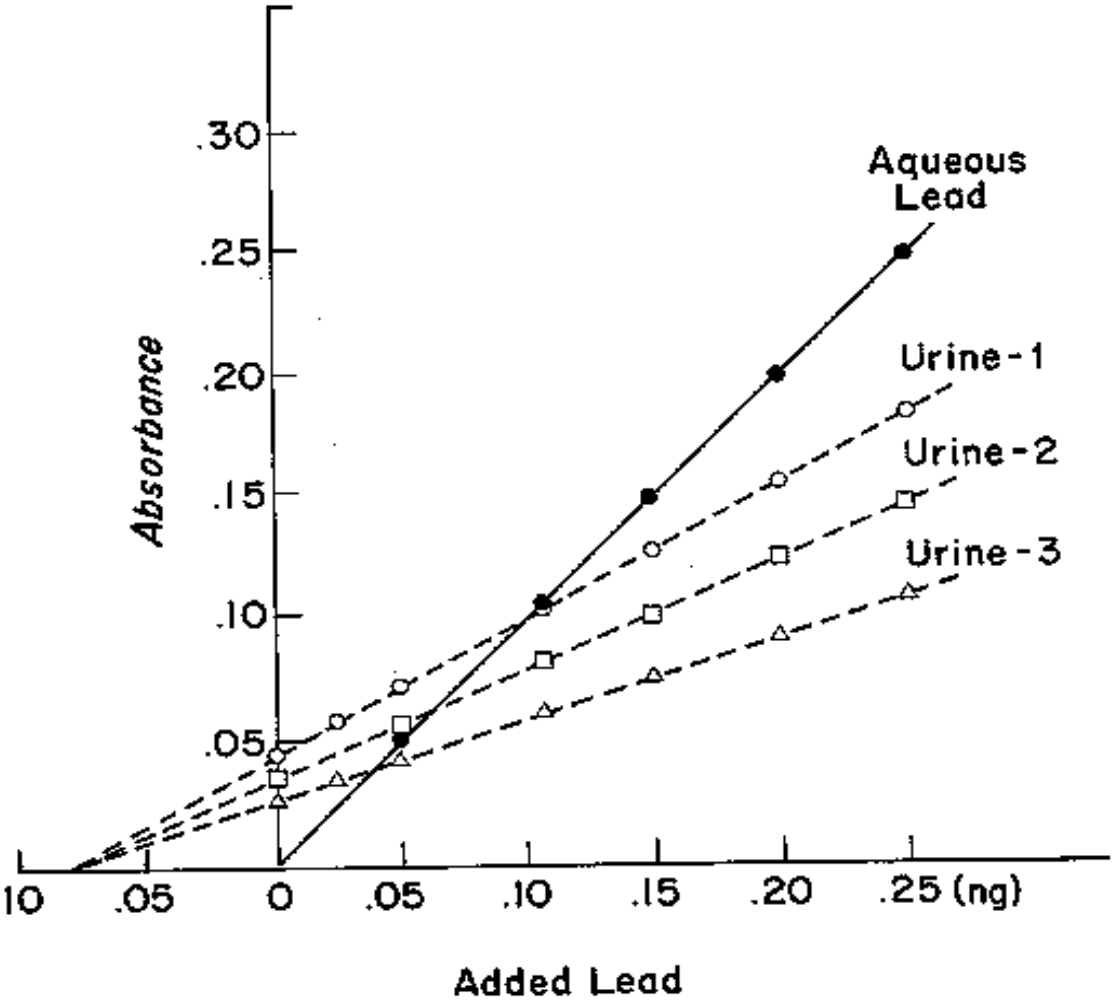

Figure 1. Calibration curve for aqueous lead standards and urine standard-addition.

M-02

PRECIPITATION AND LAKE WATER SAMPLES - PHYSICAL AND CHEMICAL MEASUREMENTS

INTRODUCTION

The physical and chemical parameters in precipitation and lake water samples are measured directly with a number of instruments. Some of the measurements are described here, while the determination of trace metals and anions may be found in other procedures in this Manual (see Anions-01-E and M-03). The measurements described here are: conductivity, pH, Na, Mg, K, and Ca. If both pH and conductivity measurements are to be made on the same sample aliquot, the conductivity measurement must be made first.

Conductivity Measurements

APPLICATION

This procedure has been applied to precipitation and lake water samples. The specific conductance (reciprocal of the electrical resistance) is measured using a conductivity cell and conductivity bridge.

SPECIAL APPARATUS

1. Conductivity bridge (available from chemical supply companies, e.g., Barnstead Model PM-70CB).

2. Conductivity cell (available from chemical supply companies, e.g., Yellow Springs Institute Model 3417, cell constant 1.0 cm^{-1}).

3. Disposable polystyrene beakers, 50 mL (available from chemical supply companies, e.g., Fisher 02-544-38).

SPECIAL REAGENTS

1. 0.02M KCl: dissolve 1.4912 g of KCl in 1 L of water. This solution has a specific conductance of 294 µS.

2. High purity water (2-20 MΩ resistance).

DETERMINATION

1. Prepare several standards ranging from 10-294 µS by serial dilution of the 0.02M KCl stock solution.

2. Immerse the conductivity cell for 3-5 min in at least 20 mL of high purity water that is contained in a 50-mL disposable beaker. The cell should not touch the plastic beaker. At least 20 mL of solution is necessary for accurate measurement.

3. Remove the cell from the water and dry using a tissue. Care should be taken **not to touch** the cell with bare hands, which can adversely affect subsequent measurements.

4. Measure each standard, rinsing with deionized water, and drying the cell after each reading. Start with the multiplier knob of the conductivity bridge at the µS X1 position. If the reading is off scale, use a higher multiplier scale position until the meter is on scale. Null the meter using the digital switch. The conductivity reading is the product of the digital switch valve and the multiplier scale setting.

5. Plot the conductance readings obtained in Step 4 against their expected conductances. The plot will be a straight line and can be described by the equation:

$$y = mx + b \quad (1)$$

where m is the slope of the line, x the expected conductance, y the conductivity meter reading, and b the y-intercept. The intercept represents the specific conductance of the deionized water. If m is between 0.9-1.1, proceed to Step 6. If m is outside this range, the conductivity cell electrode should be replatinized according to the manufacturer's instructions.

6. Measure each sample, rinsing with deionized water and drying the cell after each reading.

7. For each conductivity reading (y), compute the specific conductance (x) using Equation 1, and intercept value (b) calculated in Step 5.

Note:

All solutions must be at room temperature prior to measurement. At least 20 mL of each solution should be available for each measurement. The conductivity cell should be stored in deionized water when not in use.

pH Measurements

APPLICATION

This procedure is applicable to precipitation and lake water samples. The low ionic strength (often <20 µS conductance) and poor buffering capacities of these samples require precautions in calibration and handling of the electrode to obtain accurate pH values.

The pH of a solution is measured using either glass sensing and reference electrodes or a combination electrode coupled to a pH meter.

SPECIAL APPARATUS

1. pH meter (available from chemical supply companies, e.g., Orion Research Model 901).

2. Combination sensing/reference electrode (available from chemical supply companies, e.g., Orion Research Model 810200).

3. Glass sensing electrode (Orion Research Model 4153-H30; A. H. Thomas).

4. Reference electrode (Orion Research Model 4153-40; A. H. Thomas).

5. Disposable polystyrene beakers, 50 mL (available from chemical supply companies, e.g., Fisher Scientific 02-544-38).

SPECIAL REAGENTS

1. Buffer solution, 4.00 ± 0.02; potassium acid phthalate (available from chemical supply companies, e.g., Fisher Scientific SO-B-101).

2. Buffer solution, 5.00 ± 0.02; potassium acid phthalate (available from chemical supply companies, e.g., Fisher Scientific SO-B-102).

3. Buffer solution, 7.00 ± 0.02; potassium phosphate monobasic (available from chemical supply companies, e.g., Fisher Scientific SO-B-112).

4. Water, high purity (2-20 MΩ).

DETERMINATION

1. Rinse the electrode thoroughly with the high purity deionized water. Dry the tip by gently dabbing it with a tissue. Great care should be taken to prevent scratching the electrode surface.

2. Check to see that the internal filling solution (3M KCl) is within ~ 1 cm of the fill hole. If not, remove the band and add additional filling solution.

3. Remove the band covering the fill hole. Immerse the electrode in pH 7.00 buffer so that the solution completely covers the ceramic frit and the electrode does not touch the plastic beaker. (Twenty milliliters of sample in a 50-mL disposable plastic beaker is necessary for accurate measurements.)

4. To calibrate the meter, turn the **Mode Switch** on the Model 901 meter to pH. Set the **Standard Value Switch** to read the value of the buffer. The meter will display the response in mV. Wait until the reading on the unit stabilizes (the value should not vary more than 0.1 mV in a 1-min interval). Then press the **Set Concentration** button on the right of the meter. The meter will now display the value of the buffer to four significant figures, 7.000.

5. Carefully rinse the electrode with deionized water and dry.

6. Immerse the electrode in the pH 4.00 buffer solution.

7. Allow the pH reading to stabilize; the reading should vary no more than ± 0.002 pH units in a 1-min interval. Using the **Slope Switch**, adjust the pH reading to 4.000.

8. Carefully rinse the electrode with deionized water and dry.

9. Immerse the electrode in the pH 5.00 buffer solution.

10. The pH value that is displayed should be 5.000 ± 0.005 and should be stable for 1 min. If these criteria are not met, the entire calibration procedure should be repeated. If a second attempt does not provide these results, consult both the electrode and meter manual for further assistance.

11. Proceed to analyze the samples, carefully rinsing and drying the electrode between each reading. For samples below pH 5.000, the readings should be stable to ± 0.002 pH units in <5 min. Above pH 5.000 and in solutions of low ionic strength (<20 µS

specific conductance), longer periods may be required to achieve a stable reading. The pH reading should be stable to ± 0.002 pH units before the value is recorded.

12. Measure the pH 5.00 buffer after every five samples are measured. If the value has changed by more than 0.01 pH units, return to Step 3 and recalibrate.

Note:

At least 20 mL of solution is required for each pH measurement. Although the Orion Model 810200 combination electrode is designed to accommodate solutions of varying temperature without significant changes in pH, it is desirable to maintain all solutions at room temperature. If electrodes other than the Orion Model 810200 are used, changes in the temperature of the solutions can affect the pH. Store the electrode in pH 5 buffer with the band covering the fill hole when not in use.

Sodium

APPLICATION

This procedure is applicable for aqueous solutions containing Na in concentrations from 0.01 µg mL^{-1} to brines. Sodium is determined directly by atomic absorption (AA) or atomic emission (AE) spectrometry. A preliminary sample measurement is made to estimate the concentration range. Standard solutions of similar chemical composition bracketing this value are prepared within the linear calibration range. Comparison of the sample to the standards gives the actual Na concentration.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single slot and an air/acetylene atomizer burner or equivalent.

2. Printer.

3. Sodium hollow cathode lamp (Perkin Elmer).

SPECIAL REAGENTS

1. Sodium stock solution (100 µg mL^{-1}) - weigh out 0.254 g of analytical reagent grade NaCl, dissolve in deionized water and dilute to 1 L in a volumetric flask.

2. Doubly-deionized water must be used throughout for sample preparation and analyses.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. Prepare a series of standard Na solutions ranging in concentration from 0.01-1.6 µg mL^{-1}.

3. If sample dilution is required, prepare at least two different dilutions of the sample.

DETERMINATION

1. Set up the spectrometer according to the measurement conditions listed in Table 1 (see Procedure M-03).

2. Measure each standard solution and sample a minimum of three times. (**Note:** Wear tinted safety glasses while performing this analysis.)

3. Prepare a calibration curve by plotting mean absorbance versus concentration for the standard solutions.

4. Read off the Na concentration of the sample from the curve.

5. Calculate the Na concentration in the original sample by correcting for any dilutions.

6. Solutions should be analyzed within 24 h of preparation to minimize changes in Na concentration due to evaporation, contamination, and other effects.

LOWER LIMIT OF DETECTION (LLD)

Atomic absorption:	Sensitivity:	20 µg L^{-1}
	Detection limit:	0.5 µg L^{-1}
Atomic emission:	Sensitivity:	5 µg L^{-1}
	Detection limit:	0.5 µg L^{-1}

Magnesium

APPLICATION

This procedure is applicable for aqueous solutions of varying Mg concentrations. Magnesium is determined directly by AA spectrometry. A preliminary sample measurement is made to estimate the concentration range. Standard solutions of similar chemical composition bracketing this value are prepared within the linear calibration range. Dilution of the sample may be required. Comparison of the sample to the standards gives the actual Mg concentration.

SPECIAL APPARATUS

Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single slot, air/acetylene atomizer burner, and a Mg hollow cathode lamp or equivalent.

SPECIAL REAGENTS

1. Magnesium stock solution (100 µg mL^{-1}) - weigh out 0.100 g of Mg ribbon, dissolve in a minimum of HCl (<5 mL) and dilute with deionized water to 1 L in a volumetric flask.

2. Doubly-deionized water must be used throughout for sample preparation and analyses.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. Prepare a series of standard Mg solutions ranging in concentrations from 0.01-0.24 µg mL^{-1}.

3. If sample dilution is required, prepare at least two different dilutions of the sample.

DETERMINATION

1. Set up the spectrometer according to the measurement conditions listed in Table 1 (see Procedure M-02).

2. Measure each standard solution and sample a minimum of three times. (**Note**: Wear tinted safety glasses while performing this analysis.)

3. Prepare a calibration curve by plotting mean absorbance versus concentration for the standard solutions.

4. Read off the Mg concentration in the sample from the curve.

5. Calculate the Mg concentration in the original sample by correcting for any dilutions.

6. Solutions should be analyzed within 24 h of preparation to minimize changes in Mg concentrations due to evaporation, contamination, and other effects.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	5 µg L^{-1}
Detection limit:	0.5 µg L^{-1}

Potassium

APPLICATION

This procedure is applicable for aqueous solutions of varying K concentrations. Potassium is determined directly by AA spectrometry. To reduce the effect of ionization of the sample in the flame, a substantial excess of Na is added to all standards and samples. A preliminary sample measurement is made to estimate the concentration range. Standard solutions of similar chemical composition bracketing this value are prepared within the linear calibration range. Dilution of the sample may be required if the sample concentration exceeds the calibration curve range. Comparison of the sample to the standards gives the actual K concentration.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single slot, air/acetylene atomizer burner, and a potassium hollow cathode lamp or equivalent.

2. Micropipette (available from chemical supply companies, e.g., Epperdorf).

SPECIAL REAGENTS

1. Potassium stock solution (100 µg mL^{-1}) - weigh out 0.191 g of oven-dried analytical reagent grade KCl, dissolve in water and dilute to 1 L in a volumetric flask.

2. Sodium stock solution (10,000 µg mL^{-1}) - weigh out 25.42 g of oven-dried analytical reagent grade NaCl, dissolve in water and dilute to 1 L in a volumetric flask.

3. Doubly-deionized water must be used throughout for sample preparation and analyses.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. Oven-dry a 10-mL volumetric flask for each sample.

3. Pipette 1.0 mL of the 10,000 µg mL^{-1} Na solution into each 10-mL volumetric flask and add a known amount of sample, either by pipette or by adding sample to the calibration mark. Each sample is now in a 1000 µg mL^{-1} Na matrix.

4. Prepare a 1000 µg mL^{-1} Na stock by diluting 100 mL of the 10,000 µg mL^{-1} Na solution to volume in a 1-L volumetric flask.

5. Prepare a series of standard K solutions ranging from 0.02-0.80 µg mL^{-1} using a micropipette for the standard additions and dilute to volume with the 1000 µg mL^{-1} Na solution. This 1000 µg mL^{-1} Na solution is used as the blank in the determination.

DETERMINATION

1. Set up the spectrometer according to the conditions listed in Table 1 (see Procedure M-03).

2. Measure each standard solution and sample a minimum of three times. (**Note**: Wear tinted safety glasses while performing this analysis.)

3. Correct all standard and sample absorption values for the blank.

4. Prepare a calibration curve by plotting the corrected mean absorbances versus concentration for the standard solutions.

5. Read off the K concentration of the sample from the curve.

6. Calculate the K concentration in the original sample by correcting for any dilutions.

7. Solutions should be analyzed within 24 h of preparation to minimize changes in concentration due to evaporation, contamination, and other effects.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	40 µg L^{-1}
Detection limit:	10 µg L^{-1}

Calcium

APPLICATION

This procedure is applicable for aqueous solutions of varying Ca concentrations. Calcium is determined directly by AA or AE spectrometry. To reduce the effect of chemical suppression of the sample in the flame, a substantial excess of La is added to all standards and samples. A preliminary sample measurement is made to estimate the concentration range. Standard solutions of similar chemical composition bracketing this value are prepared within the linear calibration range. Dilution of the sample may be required if the sample concentration exceeds the calibration curve range. Comparison of the sample to the standards gives the actual Ca concentration.

SPECIAL APPARATUS

Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single slot, air/acetylene atomizer burner, and a Ca hollow cathode lamp or equivalent.

SPECIAL REAGENTS

1. Calcium stock solution (100 µg mL^{-1}) - weigh out 0.25 g of oven-dried analytical reagent grade $CaCO_3$, dissolve in a minimum of HCl (<5 mL) and dilute to 1 L in a volumetric flask.

2. Lanthanum stock solution (10,000 µg mL^{-1}) - commercially available through Spex Industries, NJ.

3. Doubly-deionized water must be used throughout for sample preparation and analyses.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. Pipette 1.0 mL of the 10,000 µg mL^{-1} La solution into each 10 mL volumetric flash and add a known amount of sample by adding sample to the calibration mark.

3. Prepare a series of standard Ca solutions ranging from 0.06-1.40 µg mL^{-1}.

4. If sample dilution is required, prepare at least two different dilutions of the sample.

DETERMINATION

1. Set up the spectrometer according to the conditions listed in Table 1 (see Procedure M-03).

2. Measure each standard solution and sample a minimum of three times. (**Note**: Wear tinted safety glasses while performing this analysis.)

3. Prepare a calibration curve by plotting mean absorbance versus concentration for the standard solutions.

4. Read off the Ca concentration in the sample from the curve.

5. Calculate the Ca concentration in the sample by correcting for any dilutions.

6. Solutions should be analyzed within 24 h of preparation to minimize changes in Ca concentration due to evaporation, contamination, and other effects.

LOWER LIMIT OF DETECTION (LLD)

Atomic Absorption:	Sensitivity:	80 µg L^{-1}
	Detection limit:	5 µg L^{-1}
Atomic Emission:	Sensitivity:	40 L^{-1}
	Detection limit:	5 L^{-1}

M-03

TRACE METALS - ATOMIC ABSORPTION AND/OR EMISSION SPECTROMETRY

INTRODUCTION

This procedure has been used to calibrate carrier solutions used for radiochemical procedures.

The instrument operational parameters, sensitivities, and limits of detection for a spectrometer are provided. The following metals, Cs, Rb, K, and Y are described separately in this procedure.

Atomic Emission Determination of Cesium

APPLICATION

This procedure has been applied to aqueous solutions of varying Cs concentrations.

Cesium is determined directly by AE spectrometry. A preliminary measurement is made to indicate the range. A large quantity of another alkali metal (1000 mg L^{-1} K as KCl) is added to all samples and standards to correct for the large fraction of Cs atoms that are ionized in the air/acetylene flame. Comparison of the sample to the standards gives the Cs concentration in the samples.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with 10.5-cm single-slot air/acetylene atomizer burner or equivalent.

2. Acetylene source.

SPECIAL REAGENTS

1. Cesium stock solution (1000 µg mL^{-1}) - weigh out 1.2670 g of CsCl. Dilute to 1 L with water.

2. KCl stock solution (10,000 µg mL^{-1}) - weigh out 19.1 g of KCl and dissolve in 1 L of water.

3. Doubly-deionized water must be used throughout for sample preparation and analysis.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. For each sample, add 5 mL of the 10,000 µg mL^{-1} KCl stock solution to a 50-mL volumetric flask.

3. Dilute to 50 mL with the sample solution.

4. If further dilutions are required, prepare each so that the K concentration in the final dilution is 1000 mg L^{-1}.

5. Prepare a minimum of two final dilutions per sample of different concentrations.

6. In a similar manner, prepare a series of Cs standard solutions that bracket the concentration range of the samples. All standards and final dilutions now contain at least 1000 mg L^{-1} K.

DETERMINATION

1. Set up the spectrometer for the flame emission spectroscopic determination of Cs according to the conditions listed in Table 1.

2. Measure each standard solution and the final sample dilutions a minimum of two times.

3. Prepare a calibration curve by plotting the mean emission value versus concentration for the standard solutions.

4. Read the Cs concentration from the curve.

5. Calculate the Cs concentration in each sample value by correcting for all dilutions.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	0.10 µg mL^{-1}
Detection Limit:	0.005 µg mL^{-1}

Atomic Emission Determination of Potassium

APPLICATION

This procedure has been applied to aqueous solutions of varying K concentrations.

Potassium is determined directly by AE spectrometry. A preliminary measurement is made to indicate the range. Comparison of the sample to the standards gives the K concentration in the samples.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single-slot air/acetylene atomizer burner or equivalent.

2. Acetylene source.

SPECIAL REAGENTS

1. Potassium stock solution (100 µg mL^{-1}) - weigh out 0.1907 g of KCl and dissolve in 1 L of water.

2. Doubly-deionized water must be used throughout for sample preparation and analysis.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. Prepare a series of standard solutions that bracket the range of K concentrations in the samples.

3. If sample dilution is required, prepare at least two different dilutions of the sample.

DETERMINATION

1. Set up the spectrometer for the flame emission spectroscopic determination of K according to the conditions listed in Table 1.

2. Measure each standard solution and sample dilution a minimum of two times.

3. Prepare a calibration curve by plotting the mean emission value versus concentration for the standard solution.

4. Read the K concentration from the curve.

5. Correct each sample value for dilutions if necessary.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	2 µg L^{-1}
Detection Limit:	0.5 µg L^{-1}

Atomic Emission Determination of Rubidium

APPLICATION

This procedure has been applied to aqueous solutions of varying Rb concentrations.

Rubidium is determined directly by AE spectrometry. A preliminary measurement is made to indicate the range. A large quantity of another alkali metal (1000 mg L^{-1} K as KCl) is added to all samples and standards to correct for the large fraction of Rb atoms that are ionized in the air/acetylene flame. Comparison of the sample to the standards gives the Rb concentration in the samples.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 10.5-cm single-slot air/acetylene atomizer burner or equivalent.

2. Acetylene source.

SPECIAL REAGENTS

1. Rubidium stock solution (1000 µg mL^{-1}) - weigh out 1.4150 g of RbCl. Dilute to 1 L with water.

2. Potassium chloride stock solution (10,000 µg mL^{-1}) - weigh out 19.1 g of KCl and dissolve in 1 L of water.

3. Doubly-deionized water must be used throughout for sample preparation and analysis.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. For each sample, add 5.00 mL of the 10,000 µg mL^{-1} KCl stock solution to a 50-mL volumetric flask.

3. Dilute to 50 mL with the sample solution.

4. If further dilutions are required, prepare each so that the K concentration in the final dilution is 1000 mg L^{-1}.

5. Prepare a minimum of two final dilutions per sample of different concentrations.

6. In a similar manner, prepare a series of Rb standard solutions that bracket the concentration range of the samples. All standards and final sample dilutions now contain at least 1000 mg L^{-1} K.

DETERMINATION

1. Set up the spectrometer for the analysis of Rb by flame emission spectroscopy according to the conditions listed in Table 1.

2. Measure each standard solution and the final sample dilutions a minimum of two times.

3. Prepare a calibration curve by plotting the mean emission value versus concentration from the curve.

4. Read the Rb concentration from the curve.

5. Calculate the Rb concentration in each sample value by correcting for all dilutions.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	30 µg L^{-1}
Detection Limit:	2 µg L^{-1}

Atomic Emission Determination of Yttrium

APPLICATION

This procedure has been applied to aqueous solutions of varying Y concentrations.

Yttrium is determined directly by AA spectrometry. A preliminary measurement is made to indicate the range. A large quantity of another alkali metal (1000 mg L^{-1} K as KCl) is added to all samples and standards to correct for the large fraction of Y atoms that are ionized in the nitrous oxide/acetylene flame. Comparison of the sample to the standards gives the Y concentration in the samples.

SPECIAL APPARATUS

1. Atomic absorption spectrometer - Perkin Elmer Model 5000 equipped with a 5.3-cm single-slot nitrous oxide/acetylene atomizer burner or equivalent.

2. Acetylene source.

3. Nitrous oxide source with heating tape around gas regulator.

SPECIAL REAGENTS

1. Yttrium stock solution (1000 µg mL^{-1}) - weigh out 1.27 g of Y_2O_3. Dissolve in a minimum volume of HCl and dilute to 1 L with water.

2. KCl stock solution (10,000 µg mL^{-1}) - weigh out 19.1 g of KCl and dissolve in 1 L of water.

3. Doubly-deionized water must be used throughout for sample preparation and analysis.

SAMPLE PREPARATION

1. Clean all glassware by rinsing several times with 1:1 HNO_3, followed by copious rinsing with doubly-deionized water.

2. For each sample, add 5 mL of the 10,000 µg mL^{-1} KCl stock solution to a 50-mL volumetric flask.

3. Dilute to 50 mL with the sample solution.

4. If further dilutions are required, prepare each sample so that the K concentration in the final dilution is 1000 mg L^{-1}.

5. Prepare a minimum of two final dilutions per sample of different concentrations.

6. In a similar manner, prepare a series of Y standard solutions that bracket the concentration range of the samples. All standards and final sample dilutions now contain at least 1000 mg L^{-1} K.

DETERMINATION

1. Set up the spectrometer for the flame emission spectroscopic determination of Y using the conditions listed in Table 1.

2. Measure each standard solution and the final sample dilutions a minimum of two times.

3. Prepare a calibration curve by plotting the mean absorption value versus concentration for the standard solutions.

4. Read the Y concentration from the curve.

5. Calculate the Y concentration in each sample value by correcting for all dilutions.

LOWER LIMIT OF DETECTION (LLD)

Sensitivity:	2000 µg L^{-1}
Detection Limit:	200 µg L^{-1}

TABLE 1

TRACE ELEMENT ANALYSIS BY ATOMIC ABSORPTION OR
ATOMIC EMISSION SPECTROMETRY OF TRACE METALS

Element	Mode (AA or AE)	Flame Gases (Press./Press.)	Modifier	Wavelength (nm)	Slit (nm)	Source HCl (mA)*, EDL (W)**	Sensitivity ($\mu g\ mL^{-1}$)	LLD ($\mu g\ mL^{-1}$)
Al	AA	N^{+} - 60/40	-	309.3	0.7	HCL:10	0.500	0.100
Ca	AA	A^{++} - 30/60	-	422.7	0.7	HCL:20	0.080	0.005
	AE	A^{++} - 30/60	-	422.7	0.7	-	0.040	0.005
	AA	A^{++} - 30/60	1000 mg L^{-1} La	422.7	0.7	HCL:20	0.040	0.002
	AE	A^{++} - 30/60	1000 mg L^{-1} La	422.7	0.7	-	0.020	0.002
	AA	N^{+} - 60/40	-	422.7	0.7	HCL:20	0.060	0.005
	AE	N^{+} - 60/40	-	422.7	0.7	-	0.030	0.005
Co	AA	A^{++} - 35/60	-	240.7	0.2	HCL:20	0.200	0.040
Cd	AA	A^{++} - 35/60	-	228.8	0.7	HCL:10	0.020	0.002
Cu	AA	A^{++} - 30/60	-	324.7	0.7	HCL:15	0.050	0.005
Cs	AE	A^{++} - 35/60	1000 mg L^{-1} K	852.1	4.0	-	0.100	0.005
Fe	AA	A^{++} - 35/60	-	248.3	0.2	HCL:20	0.100	0.020
K	AA	A^{++} - 35/60	1000 mg L^{-1} Na	766.5	4.0	HCL:12	0.040	0.010
	AE	A^{++} - 35/60	-	766.5	4.0	-	0.002	0.0005
Mg	AA	A^{++} - 35/60	-	285.2	0.7	HCL:10	0.005	0.0005
Mn	AA	A^{++} - 35/60	-	279.5	0.2	HCL:10	0.040	0.004
Na	AA	A^{++} - 35/60	-	589.0	1.4	HCL:8	0.020	0.0005
	AE	A^{++} - 35/60	-	589.0	1.4	-	0.005	0.0005
Ni	AA	A^{++} - 35/60	-	232.0	0.2	HCL:20	0.100	0.020
Pb	AA	A^{++} - 35/60	-	217.0	0.7	HCL:10	0.200	0.040
	AA	A^{++} - 35/60	-	217.0	0.7	HCL:10	0.200	0.040
	AA	A^{++} - 35/60	-	283.3	0.7	HCL:10	0.400	0.060
	AA	A^{++} - 35/60	-	283.3	0.7	HCL:10	0.400	0.060
Rb	AE	A^{++} - 35/60	1000 mg L^{-1} K	780.0	4.0	-	0.030	0.002
Se	AA	A^{++} - 35/60	1000 mg L^{-1} Ni	196.0	2.0	ELD:5W	0.400	0.100
Sr	AA	A^{++} - 35/60	1000 mg L^{-1} La	460.7	0.14	HCL:20	0.200	0.040
V	AA	N^{+} - 60/40	-	318.4	0.7	HCL:35	0.400	0.100
Zn	AA	A^{++} - 30/60	-	213.9	0.7	HCL:15	0.020	0.002
Y	AA	N^{+} - 60/40	1000 mg L^{-1} K	410.9	0.2	HCL:30	2.00	0.200

*HCL = hollow cathode lamp
**EDL = electrodeless discharge lamp

Notes:
$N^{+} = N_2O/C_2H_2$
$A^{++} = Air/C_2H_2$

Sensitivity: The concentration of the element being analyzed in $\mu g\ mL^{-1}$ that generates 1% absorption (0.0044 absorbance units).

Detection Limit: The concentration of the element being analyzed in $\mu g\ mL^{-1}$ that generates a signal equal to twice the instrument background noise level.

4.5 RADIOCHEMICAL

4.5.1 SCOPE

Described in this section are the radiochemical procedures currently not in use at EML. These procedures have been constantly updated for the past 40 years to reflect current separation technology and measurement techniques. The radiochemical procedures are usually written for a distinct environmental matrix since chemical interferences and contamination levels vary according to sample type.

4.5.4 Radiochemical

Americium

Am-03-RC

AMERICIUM IN WATER, AIR FILTERS, AND TISSUE

APPLICATION

This procedure is applicable to *in vivo* determination of americium in tissue and also to environmental determination of americium in air filter and water samples.

Americium is leached from the sample and simultaneously equilibrated with ^{243}Am tracer. Americium is collected with a calcium oxalate coprecipitation and isolated and purified by organic extraction and ion exchange. The americium is electrodeposited on a platinum disc and the ^{241}Am plus tracer ^{243}Am are resolved by α spectrometry.

SPECIAL APPARATUS

1. Virgin platinum discs - 17.6 mm ID x 0.00127 mm mirror finish on one side.

2. Plating cells - see Specification 7.16, Vol. I.

3. Electrolysis electrode - see Specification 7.15, Vol. I.

4. Electrodeposition apparatus - see Specification 7.16, Vol. I.

5. Ion exchange columns - see Specification 7.5 and Procedure Pu-11-RC, Vol. I.

6. Solid-state α spectrometer - see Procedure A-01-R, Vol. I.

SPECIAL REAGENTS

1. ^{243}Am tracer solution, about 0.2 Bq g^{-1} in dispensing bottle.

2. Calcium carrier solution, 40 mg mL^{-1} - dissolve 236 g $Ca(NO_3)_2 \cdot 4H_2O$ in 15% HNO_3 and dilute to 1 L.

3. Iron carrier solution, 10 mg mL^{-1} - dissolve 144 g $Fe(NO_3)_3$ in 1:99 HNO_3 and dilute to 1 L.

4. Oxalic acid wash solution - dissolve 10 g oxalic acid in 1 L of H_2O, adjust pH to 3.0.

5. Bio-Rad AG 1-x4 resin (100-200 mesh) - see Specification 7.4, Vol. I.

6. 50% HDEHP (Di(2-ethylhexyl)phosphoric acid) - dissolve 500 mL HDEHP in 500 mL of toluene.

7. 0.1N HCl/5% NaCl solution - dissolve 50 g NaCl in 1 L of H_2O containing 8 mL of HCl.

8. 60% ethanol/40% 6N HNO_3 solution - mix 600 mL of ethanol with 400 mL of 6N HNO_3 slowly. Store in a cool place.

9. 75% methanol/25% 6N HNO_3 solution - slowly mix 750 mL of methanol with 250 mL of 6N HNO_3. Store in a cool place.

10. Methyl red indicator solution - dissolve 100 mg of methyl red in 65 mL of ethanol and dilute to 100 mL with H_2O.

SAMPLE PREPARATION

A. Air filters.

1. Place a glass fiber filter in a 100 mL Teflon beaker. Add a known amount (between 0.01 - 0.02 Bq) of ^{243}Am tracer solution, and 1 mL of Fe carrier solution.

2. Add about 30-mL of HNO_3 and enough HF to dissolve the glass fiber filter. Wet ash with HNO_3.

3. Bring to near dryness on a medium temperature hot plate, remove and cool.

4. Dissolve in a minimum of HCl and dilute to about 30-mL with H_2O.

5. Transfer to a 90-mL centrifuge tube and adjust the pH to 8 with NH_4OH.

6. Centrifuge and discard the supernate.

7. Dissolve the precipitate in HNO_3, transfer to a 250-mL beaker and proceed with **Determination**.

B. Water.

1. Transfer 1 L of H_2O to a 1500-mL beaker. Evaporate to near dryness Wet ash with HNO_3.

2. Add a known amount (between 0.01 - 0.02 Bq) of ^{243}Am tracer solution and 1 mL of iron carrier solution.

3. Add 100 mL of HCl, transfer to a 250 mL beaker and evaporate to near dryness on a medium hot plate.

4. Dissolve in a minimum of HCl and dilute to about 30 mL with water.

5. Transfer to a 90-mL centrifuge tube and adjust the pH to 8 with NH_4OH.

6. Centrifuge and discard the supernate.

7. Dissolve the precipitate in HNO_3, transfer to a 250-mL beaker and proceed with the steps in **Determination**.

C. Tissue.

1. Weigh 20 g of freeze-dried tissue into a 1 L beaker.

2. Add a known amount (between 0.01 - 0.02 Bq) of ^{243}Am tracer solution.

3. Add 300 mL of HNO_3 and wet ash with HNO_3 and H_2O_2 until all organic matter is eliminated.

4. Evaporate to near dryness, then cool.

5. Add 8 mL of calcium carrier solution and heat gently.

6. Dilute to 400 mL and add 18 g (or 45 g L^{-1}) of granular oxalic acid.

7. With stirring, add NH_4OH until the pH is 3.2. Stir for an additional 20 min.

8. Cool the sample for at least 1 h in a cold water bath.

9. Filter by gravity over a 24 cm diameter Whatman No. 42 filter paper. Wash with oxalic acid wash solution. Discard the filtrate and washings.

10. Return the filter to the beaker and wet-ash with HNO_3.

11. Repeat the precipitation filtration and wet-ashing. (Repeat again until the filtrate is colorless).

12. Transfer to a 250-mL beaker and evaporate to dryness.

13. Dissolve in a minimum of HCl and dilute to about 200 mL. Adjust the pH to 8 with NH_4OH.

14. Warm gently, then filter onto a 12.5 cm Whatman No. 42 filter paper. Wash the precipitate with H_2O and discard the filtrate.

15. Return the filter to the beaker and wet ash with HNO_3. Proceed with the steps in **Determination**.

DETERMINATION

1. Dissolve the residue in 20 mL of HNO_3, add 20 mL of water and stir. Add 200 mg of $NaNO_2$. Heat until the evolution of nitrogen oxides ceases.

2. Cool to room temperature. Pass through an ion exchange column (15 mL Bio-Rad AG 1-X4 resin) which has been conditioned with 130 mL of 1:1 HNO_3 (see Note). Collect the effluent in a 250-mL beaker.

3. Wash with 100 mL of 1:1 HNO_3. Collect the washings in the 250-mL beaker, evaporate the combined effluent and washings to dryness and evaporate the combined effluent and the washings to dryness.

4. Wet ash the residue with 10 mL of HNO_3, convert to HCl, and finally dissolve the converted residue in 40 mL of HCl.

5. Pass the sample through a column (15 mL Bio-Rad AG 1-X4) which has been conditioned with 130 mL of HCl. Wash with 100 mL of HCl. Collect effluent and washings in a 250-mL beaker and evaporate to dryness.

6. Wet ash in 10 mL of HNO_3.

7. Dissolve in 15 mL of HNO_3 and cool for 1/2 h in a cold water bath.

8. Adjust the pH to 3.0 by slowly adding NH_4OH (~10 mL).

9. Transfer to a 250-mL separatory funnel, add 100 mL of 50% HDEHP in toluene and shake for 5 min.

10. Allow to settle and discard the aqueous (lower) phase.

11. Wash twice with 60 mL of 0.1 N HCl/5% NaCl. Shake for 5 min, allow to settle and discard the aqueous (lower) phase.

12. Add 30 mL of HCl, shake for 5 min, allow to settle for at least 1 h, and collect the aqueous (lower) phase in a 250-mL beaker. Discard the organic phase.
13. Evaporate to dryness and wet ash with 10 mL of HNO_3.

14. Dissolve sample in 12 mL of 6N HNO_3 with heating. Cool for 0.5 h in a cold water bath, add 18 mL of ethanol and mix thoroughly.

15. Pass the sample through a column (15 mL Bio-Rad AG 1-X4) which has been conditioned with 130 mL of 60% ethanol/40% 6N HNO_3.

16. Wash with 60 mL 75% methanol/25% 6N HNO_3. Discard the effluent and washings.

17. Elute with 60 mL of 1:4 HNO_3 and collect the eluate in a 250-mL beaker.

18. Evaporate to dryness, and wet ash in HNO_3 with H_2O_2.

19. Evaporate to dryness and electroplate according to Electrodeposition of the Actinides: Mitchell Method, Procedure G-01, Vol. I.

Note:

Preparation of ion exchange columns. Position a plug of glass wool at the base of the column. Rinse the column with 130 mL of H_2O. Transfer 15 mL of wet, settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column, and allow it to settle. Place a second plug of glass wool on top of the resin and allow the water level to reach the top of the upper plug. Condition with the appropriate reagents.

Am-05-RC

AMERICIUM IN WATER AND AIR FILTERS

APPLICATION

This procedure is applicable to water and air filters. Americium and plutonium tracers are added to the sample and a procedure for plutonium, appropriate to the matrix, is followed. The last step in each procedure will be the ion-exchange technique for the purification of plutonium (see Procedure Pu-11-RC. Vol. I). The eluate from Step 4 is combined with the eluate from Step 8. Americium is coprecipitated with calcium oxalate, followed by coprecipitation with iron hydroxide. The acidified iron hydroxide solution is loaded onto an ion-exchange column to assure a complete removal of any traces of plutonium, followed by another ion-exchange column designed to remove iron. The eluate from the last column is evaporated, converted to HCl and microprecipitated on NDF_3 and the ^{241}Am plus the ^{243}Am tracer are resolved by α spectrometry.

SPECIAL APPARATUS

1. Ion-exchange columns - see Specification 7.5, Vol. I.

SPECIAL REAGENTS

1. ^{243}Am tracer solution, about 0.20 Bq g^{-1}, in a dispensing bottle.

2. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4, Vol. I.

3. Bio-Rad AG 1-X8 resin (50-100 mesh) - see Specification 7.4, Vol. I.

4. Calcium carrier solution, 100 mg Ca mL^{-1} - dissolve 25 g $CaCo_3$ in a minimum of HNO_3 and dilute to 100 mL.

5. Iron carrier solution, 100 mg Ca mL^{-1} - slowly heat 100 g of iron powder in 500 mL HCl until reaction ceases. Carefully and slowly add 100 mL HNO_3 while stirring. Cool and dilute to 1 L.

6. Oxalate wash solution - dissolve 10 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) to make 1 L of solution (~1% solution).

SAMPLE PREPARATION

1. Combine eluates from Steps 4 and 8 from Pu-11-RC, Vol. I, in a beaker. Evaporate to dryness. Dissolve the residue in 5 mL 7.5M HNO_3, add 45 mL H_2O and stir.

2. Add 1 mL of Ca carrier solution (100 mg Ca) and 2.5 g (50 g L-1) oxalic acid to the sample while stirring with a magnetic stirrer.

3. Adjust the pH of the solution to 2.5-3.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove magnetic stirrer.

4. Cool and let stand overnight or for more than 6 h. Check for completeness of precipitation using a drop of saturated oxalic acid solution.

5. Aspirate (or decant) as much liquid as possible without disturbing the precipitate. Transfer precipitate to a 250-mL centrifuge bottle using oxalate wash solution. Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.

6. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount of HNO3 and transfer the solution quantitatively to a beaker. Heat to destroy the oxalate ion.

7. Dissolve the wet-ashed residue in 5 mL of 7.5M HNO_3 and transfer to a 40-mL centrifuge tube, using H_2O to complete transfer and dilute to 25 mL of solution. Warm the solution in a 90° hot water bath and add 0.1 mL iron carrier solution (10 mg Fe).

8. With the centrifuge tube in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH4OH while stirring with a glass rod. Allow solution to digest in hot water bath for 20 min.

9. Cool in a cold water bath, rinse and remove the glass rod. Centrifuge for 10 min at 2000 rpm.

10. Decant (or aspirate) and discard the supernate. Add 5 drops HCl to dissolve the $Fe(OH)_3$ pellet followed by 25 mL H_2O. Heat the solution in a hot water bath.

11. Repeat Steps 8, 9 and 10 three times. Redissolve the final precipitate in 7.5M HNO_3.

12. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL 7.5M HNO_3 and evaporate to dryness again.

13. Dissolve the dry residue immediately in 40 mL 7.5M HNO_3. Cool in an ice-water bath. Add 0.6-1.0 g $NH_2OH{\cdot}HCl$, dissolve and let react for 15 min. Heat on low temperature hot plate to decompose unreacted $NH_2OH{\cdot}HCl$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 7.5M HNO_3 ion-exchange column (see **Note 1**). Adjust the rate of elution to ~0.5 mL min-1. Collect the effluent in a 400-mL beaker. Wash with 150 mL 7.5M HNO_3 and collect the effluent in the 400-mL beaker.

14. Evaporate the sample to dryness and treat several times with small volumes of HCl. Dissolve the final residue in 30 mL of HCl. Pass this solution through a 12M HCl ion-exchange column (see **Note 2**). Collect the effluent in a 250-mL beaker. Wash with 100 mL of HCl, and collect in the 250-mL beaker.

15. Evaporate to dryness. Dissolve the residue in 1-2 mL 1M HCl.

16. See Procedure G-03, Vol. I, for microprecipitation source preparation for α spectrometry.

17. Submit the sample for α spectrometry measurement.

Notes:

1. Preparation of 7.5M HNO_3 Column. Position a plug of glass wool at the base of a small column (i.d. 11 mm). Transfer 10 mL of wet settled Bio-Rad AG-X8 resin (50-100 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H_2O to reach the level of the upper plug. Wash the column with 40 mL of H_2O, followed by 300 mL of 7.5M HNO_3, passed through the resin bed in 50-mL portions. Allow the level of each portion to reach the top of the upper plug. The conversion of the resin is complete if the effluent from the column tests negative for Cl^- using a dilute silver nitrate solution.

2. Preparation of HCl Column. Position a plug of glass wool at the base of a small column (i.d. 11 min). Transfer 10 mL of wet settled Bio-Rad AG-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H2O level to reach the level of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the level of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass plug. Make sure to run this column in a vented hood.

DATA PROCESSING AND ANALYSIS

For α spectrometry measurements, see A-01-R, Vol. I.

Tritium

Environmental Measurements Laboratory
U. S. Department of Energy

^{3}H-01-RC

TRITIUM IN WATER - ACID ELECTROLYSIS

APPLICATION

This procedure is applicable to liquid water samples obtained by total distillation. The lower limit of detection is 20 ^{3}H units (T.U. = ~ .12 Bq L^{-1}), about 2.5 Bq L^{-1} for a 100-min count. If the ^{3}H content is lower than 15-20 T.U., Procedure ^{3}H-02 may be used, but this procedure is much faster for ^{3}H activities >30 T.U.

This is a modification of the procedure developed by Frank Cosalito of New York University. The sample is first completely distilled in the presence of $KMnO_4$ to eliminate solids and organic matter. The sample is then enriched by electrolysis in an acid medium (H_2SO_4) at high current for about 40 h to reduce the initial volume of 50 mL to about 6-8 mL. The final volume is determined on a known aliquot by titration of the H_2SO_4. The activity of the sample is determined on an aliquot by liquid scintillation counting. The degree of ^{3}H enrichment is determined by a calibration of enrichment against volume reduction.

SPECIAL APPARATUS

1. Electrolysis cells - see Specification 7.20, Vol. I.

2. Vacuum distillation apparatus.

3. Liquid scintillation counter.

SPECIAL REAGENTS

1. Scintillation solution - Aqua Fluor (Packard Instrument Co., 2200-T Warrensville Rd., Downers Grove, IL 60515).

2. Standardized 0.02N NaOH solution.

3. Phenolphtalein indicator solution - 0.1%.

SAMPLE PREPARATION

A. Liquid samples.

1. Transfer the sample to a 1000-mL distillation flask (not more than 800 mL at one time) and add about 1 g of $KMnO_4$.

2. Distill to dryness, then bake the distillation flask.

3. Store the distilled sample in an air-tight container until ready for enrichment.

B. Two-phase systems.

Filter the sample, then treat the filtrate as in **Liquid Samples**, or freeze-dry the sample and treat the water collected as a liquid sample.

DETERMINATION

A. Enrichment.

1. Pipette 50.0 mL of sample and 0.70 mL of H_2SO_4 into an electrolysis cell. Mix well. Prepare two standard tritiated H_2O (HTO) solutions and two blanks (low ^{3}H content H_2O) in the same way for each batch of samples.

2. Withdraw a 1.0-mL aliquot and dilute to 10 mL with water in a volumetric flask. Reserve for determination of the initial H_2SO_4 normality as required for measuring the volume reduction factor.

3. Place the electrolysis cells in a cell holder in a cooling bath maintained between 2° and 3°C.

4. Connect the electrolysis cells to a constant current power supply, observing proper polarity.

5. Adjust the current to 3 A and electrolyze until the volume is reduced to ~ 6 mL (electrolysis proceeds at ~ 1 mL h^{-1}).

6. When the electrolysis is completed, place stoppers on the cells and seal the capillary glass tubes holding the electrodes with putty or similar material to avoid exchange of the enriched sample with atmospheric moisture.

7. Transfer a 1.0-mL aliquot of the enriched sample to a 10-mL volumetric flask and dilute to 10 mL with water. Reserve this solution to determine the final volume.

8. Set up the electrolysis cell for vacuum distillation with a trap to collect the distillate.

9. Cool the trap in liquid N_2, connect the vacuum, and completely distill the enriched sample from the cell.

B. Measurement.

1. Pipette a suitable aliquot (usually 2 mL) of the distillate into a polyethylene liquid scintillation vial containing 15 mL of scintillator solution.

2. Load the samples into the counter and allow to adapt to dark and cool.

3. Set counter controls for optimum counting conditions.

4. With each batch of samples, count two standards prepared from a NIST tritiated H_2O standard. The counting efficiency is determined by the channel ratio and external standard counting techniques.

5. Count samples, standards, and blanks at least twice each. Subtract the blank count rate, compute the counter efficiency and calculate the activity for the total sample.

C. Volume determination.

1. Transfer the two volumetric flasks reserved as in the **Enrichment Section** to individual 125-mL Erlenmeyer flasks.

2. Dilute with water to about 15-20 mL, washing down the sides of the flask, and add three or four drops of phenolphthalein indicator solution (0.1%).

3. Titrate with standardized 0.02N NaOH solution to a permanent pink end point. (Between 15 and 20 mL of NaOH will usually be required.)

4. Calculate the initial and final concentrations of H_2SO_4.

D. Tritium enrichment factor.

The degree of ^{3}H enrichment is proportional to the volume reduction, but not equal to it. Thus, the enrichment factor must be determined as a function of the volume reduction. This is best done with standard samples of moderate activity.

Prepare a series of electrolysis cells with aliquots of a known amount of HTO standard, and electrolyze to a range of volume reductions covering those expected in sample analyses. Carry these through the complete analysis described in **Determination.**

The volume reduction factor is,

$$X = \frac{N_f}{N_i}$$

where N_i and N_f are the initial and final H_2SO_4 normalities.

The enrichment factor is,

$$Y = \frac{C_f}{C_i}$$

where C_f and C_i are the initial and final ^{3}H concentrations. If the values of X and Y determined from the standards are plotted, a straight line relationship should hold. The initial ^{3}H concentration can then be calculated from the measured volume reduction factor and the measured final ^{3}H concentration.

LOWER LIMIT OF DETECTION

Counter Efficiency	(%)	50
Counter Background	(cps)	0.1
LLD (100 min)	(Bq)	0.008

^{3}H-02-RC

TRITIUM IN WATER - ALKALINE ELECTROLYSIS

APPLICATION

This procedure has been applied to liquid samples obtained either by total distillation or by freeze-drying followed by distillation. The lower limit of detection is two ^{3}H units (T.U. = ~ .12 Bq L^{-1}), about 0.25 Bq L^{-1} for a 100-min count. If the ^{3}H content is higher than 15-20 T.U., Procedure ^{3}H-01-RC may be used.

This is a modification of the procedure developed by Ostlund and Werner (1962). The sample is first completely distilled in the presence of $KMnO_4$ to eliminate solids and organic matter. The sample is then enriched by electrolysis in a basic medium (NaOH) at high current until the total sample volume (normally 250 mL) has been reduced by a factor of 10. The current is then decreased and the electrolysis is continued to reduce the volume by an additional factor of 5 to 10. The final volume is measured by total distillation directly from the electrolysis cell. The ^{3}H activity is determined on an aliquot by liquid scintillation counting. The degree of ^{3}H enrichment is determined by a calibration of enrichment against volume reduction.

SPECIAL APPARATUS

1. Electrolysis cells - see Specification 7.20, Vol. I.

2. Vacuum distillation apparatus.

3. Liquid scintillation counter.

SPECIAL REAGENT

Scintillation solution - Aqua Fluor (Packard Instrument Co., 2200-T Warrensville Rd., Downers Grove, IL 60515).

SAMPLE PREPARATION

A. Liquid samples.

1. Transfer the sample to a 1000-mL distillation flask (not more than 800 mL at one time) and add about 1 g of $KMnO_4$.

2. Distill to dryness, then bake the distillation flask. (Many samples with appreciable impurities in the original material will require a second distillation.)

3. Store the distilled sample in an air-tight container until ready for analysis.

B. Two-phase systems.

Filter the sample, then treat the filtrate as in **Liquid Sample**, or freeze-dry the sample and treat the H_2O collected as a liquid sample.

DETERMINATION

A. Enrichment.

1. Add about 400 mg of NaOH (two average size pellets) and 5-10 mL of the sample to a clean electrolysis cell. Shake until the pellets are completely dissolved.

2. Add more sample to make the volume ~ 50 mL.

3. Insert the iron and nickel electrode assembly (the tips of the electrodes should almost touch the bottom of the well in the cell). Stopper the cell and make sure the leads to the electrodes are outside the closure.

4. Place the cell in a cell holder in a cooling bath maintained between 2° and 4°C.

5. Connect the electrolysis cell to a constant current power supply, observing proper polarity.

6. Adjust the current to 3 A and electrolyze until the volume is reduced to 25 mL.

7. Add another 25 mL of sample and repeat these additions until all of the sample has been added to the cell (electrolysis proceeds at ~ 1 mL h^{-1}). The volume after the final addition should be reduced to 25 mL.

8. Reduce the current to 0.3 A and continue the electrolysis until the volume is 2.5-4 mL. (This step typically takes 8-9 days.)

9. Discontinue the electrolysis and keep the cells closed and in the cooling bath until ready to distill. Immediately prior to distillation, bubble CO_2 gas through the sample for 3-5 min.

10. Set up the electrolysis cell for vacuum distillation with a tared trap to collect the distillate.

11. Wrap a length of heating tape around the body of the electrolysis cell and connect it to an autotransformer.

12. Apply the vacuum and distill the bulk of the sample, cooling the trap in liquid N_2.

13. Increase the applied voltage so as to heat the body of the cell progressively to ~ 150°C, and continue the distillation.

14. After about 2 h, switch off the heating current, still applying the vacuum and keeping the trap immersed in liquid N_2.

15. Disconnect the vacuum pump, remove the collection trap, thaw, and weigh.

16. Reconnect to the vacuum distillation apparatus and repeat Steps 13-15 until no further weight increase occurs.

B. Measurement.

1. Pipette a suitable aliquot (usually 2 mL) of the distillate into a polyethylene liquid scintillation vial containing 15 mL of scintillator solution.

2. Load the samples into the counter and allow to adapt to dark and cool.

3. Set counter controls for optimum counting conditions as determined from standards.

4. With each batch of samples, count two standards prepared from a NIST tritiated H_2O standard. Efficiency is also checked with the channel ratio and external standard counting.

5. With each batch of samples, 10% of the measurements should be performed using blanks prepared from low HTO H_2O.

6. Count samples, standards, and blanks at least twice each. Subtract the blank count rate, compute the counter efficiency and calculate the activity for the total sample.

C. Tritium enrichment factor.

The degree of ^{3}H enrichment is proportional to the volume reduction, but not equal to it. Thus, the enrichment factor must be determined as a function of the volume reduction. This is best done with standard samples of moderate activity.

Prepare a series of electrolysis cells with aliquots of a known standard and electrolyze to a range of final volumes covering those expected in sample analyses. Carry these through the complete analysis described above.

The volume reduction factor is,

$$X = \frac{V_i}{V_f}$$

where V_i and V_f are the initial and final volumes, the enrichment factor is,

$$Y = \frac{C_f}{C_i}$$

where C_f and C_i are the initial and final ^{3}H concentrations. If the values of X and Y determined from the standards are plotted, a straight line relationship should hold. The initial ^{3}H concentration can then be calculated from the measured volume reduction factor and the measured final ^{3}H concentration.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	50
Counter Background	(cps)	0.1
LLD (100 min)	(mBq)	0.008

REFERENCE

Ostlund, H. G. and E. Werner
"The Electrolytic Enrichment of Tritium and Deuterium for Natural Tritium Measurements"
in Tritium in Physical and Biological Sciences
International Atomic Energy Agency, Vienna (Ref. No. I-95-104) (1962)

^{3}H-03-RC

ORGANICALLY LABELED TRITIUM - COMBUSTION PROCEDURE

APPLICATION

A combustion procedure is described for the quantitative conversion of organically labeled ^{3}H to tritiated water. The procedure is applicable to biological samples including vegetation, foods, and tissues.

The determination of the ^{3}H specific activity of organic materials requires quantitative combustion to prevent the buildup of pyrolysis products and resulting isotope effects. The solution to this problem is provided by slow combustion in a specially designed chamber with a controlled atmosphere. Argon and O_2 of ultra-high purity are used for combustion. The water is collected in a manifold consisting of a series of traps immersed in a dry ice-alcohol mixture and liquid N_2.

SPECIAL APPARATUS

The combustion train consists of: 1) a gas purification system with traps containing molecular sieve (Figure 1); 2) a gas-heated combustion chamber (Figure 2); and 3) a collection manifold (Figure 3).

The purification system (Figure 1) consists of separate traps for the argon and O_2 which contain a Linde 4A molecular sieve. This gives a final purification and drying step before mixing the gases and admission to the combustion tube. In various periods of the combustion, the gases are used separately and in a 1:1 mixture.

The valve system allows for evacuation of the system, introduction of other gases or transfer to the combustion chamber. A 76 cm to 76 cm compound gauge indicates the pressure in the purification system.

The combustion chamber (Figure 2) consists of an inconel tube 135 cm x 7.6 cm with O-ring flanges on each end. The O-rings are protected by cooling coils of 1 cm copper tubing wound around each end as near to the flange as possible. The coils are connected in series to a cold water tap, and the O-rings are maintained at about room temperature throughout a combustion. The exit end of the chamber contains 30 cm of CuO in the form of a large plug prepared from copper wire sandwiched between tightly wound plugs of rolled heavy copper screen. The screen is rolled so that the plugs require forced fitting to provide good mechanical support for the finely divided copper wire. Once in place the wire screen is oxidized to CuO by burning at red heat in air.

Two Meker burners heat the CuO zone and three burners are used under the sample combustion area. The rest of the inconel tube is covered with Siltemp nonasbestos thermal barrier.

Throughout any series of combustion runs, it is advisable to maintain the CuO at 700^{o}C. Also, one burner is kept on between runs to maintain the temperature at 450^{o}C. This procedure minimizes shrinkage and settling of the plug, which can lead to channeling and incomplete combustion. The CuO temperature is monitored by a thermocouple inserted into the middle of the plug.

The collection manifold (Figure 3) consists of a series of traps for removing H_2O. The three H_2O removal traps are immersed in a dry ice-alcohol mixture, and for ^{3}H samples only, this would complete the system.

The vacuum pump is capable of evacuating to 0.01 Pa of Hg. A liquid N_2 cold trap is used in the vacuum line to assure that this pressure can be reached.

SAMPLE PREPARATION

Freeze-dry a weighed sample and reserve the H_2O fraction for ^{3}H analysis. Compress the residue into pellets weighing up to 60 g in a 2.5 cm diameter pelleting press. The compression is required to control the combustion process. Store the pellets in a desiccator. Combustion of about 100 g is required to produce 50 mL of water.

DETERMINATION

A. Combustion procedure.

System preparation.

1. Close valves 1, 3, 4, and 5 (see Figures 1 and 3). Open valve 2 to the vacuum line, crack valve 3, and pump down the combustion tube. (Too rapid evacuation may shift the CuO plug.) Open valve 3 all the way and pump for 5-10 min.

2. Close valve 2 and admit the argon slowly to atmospheric pressure, opening valve 1 and the argon tank valve. Close valve 1.

3. Pump down the collection system by opening valve 8, with all other valves closed, then open valves 7, 9, and 11. Crack valve 6 and complete pumping down the collection system to full vacuum (about 10^{-4} 0.01 Pa).

4. Close valve 9. Place the dry ice-alcohol mixture around the H_2O traps and liquid N_2 around the CO_2 traps. Continue pumping the system between valves 5 and 9.

5. Bring the CuO section of the combustion tube to 700^{o}C with the two burners.

Combustion.

1. Transfer about 50 g of pelletized sample to a 5 cm x 2 cm x 25 cm combustion boat lined with 60 mesh alundum.

2. Open the flange on the combustion tube and insert the boat as quickly as possible so that it butts against the CuO plug. Close the combustion tube. The sample is now in an argon atmosphere.

3. Crack valve 5 and wait for the pump to start gurgling, using the gauge on the combustion tube as a guide. Continue pumping throughout the combustion. Wait 5-10 min before proceeding.

4. Open the O_2 valve to obtain a 1:1 mixture of O_2 and argon. Slowly crack valve 1 and allow the gas mixture gauge pressure to drop about 1.25 cm. This is equivalent to a flow of 0.5 to 1 L min^{-1}.

5. Light the burner nearest the entrance end of the combustion tube. Bring the tube to red heat in this area and continue heating until the pressure rises. Control pressure to 55 cm vacuum or more by reducing the gas flow or removing from the burner.

6. When the pressure drops, light the middle burner, and follow the procedure in Step 5.

7. When the pressure drops, light the third burner, close off the argon supply and continue combustion with O_2, following the procedure in Step 5.

8. Continue combustion until the pressure is lowered and begins to rise. After 15-30 min, the pump should begin to gurgle and the thermocouple in the CuO plug should rise, indicating reoxidation of the plug. Allow O_2 to flow an additional 15-30 min and then close valves 1, 3, 5, 6, and 7. The water should now be retained in the trap.

B. Tritium collection.

Collect and measure the volume of water in the three water traps. Determine HTO directly or after enrichment as described in Procedure ^{3}H-01-RC or ^{3}H-02-RC.

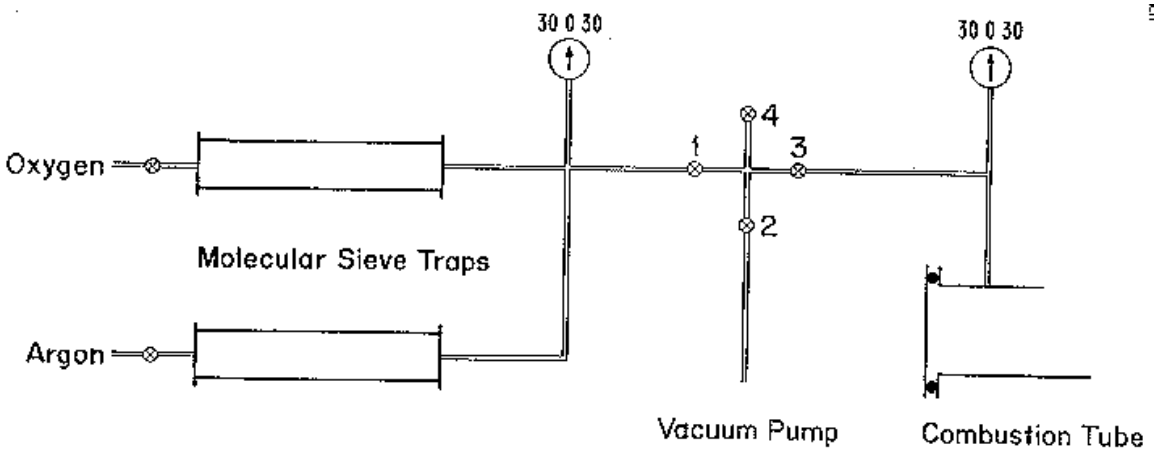

Figure 1. Gas purification system.

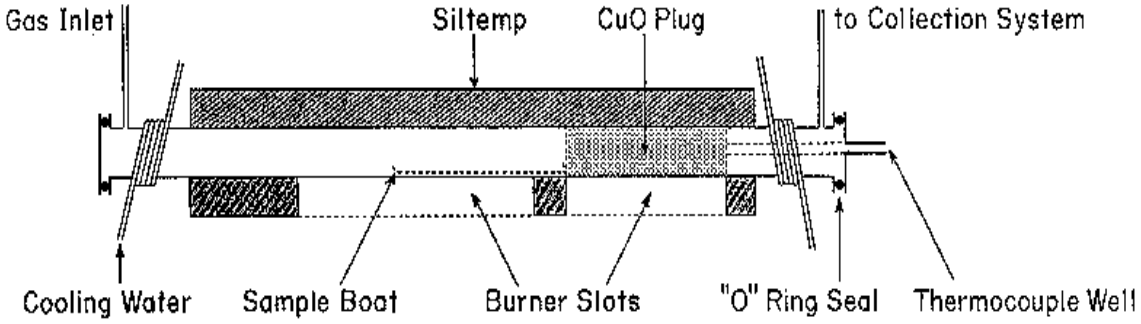

Figure 2. Combustion chamber.

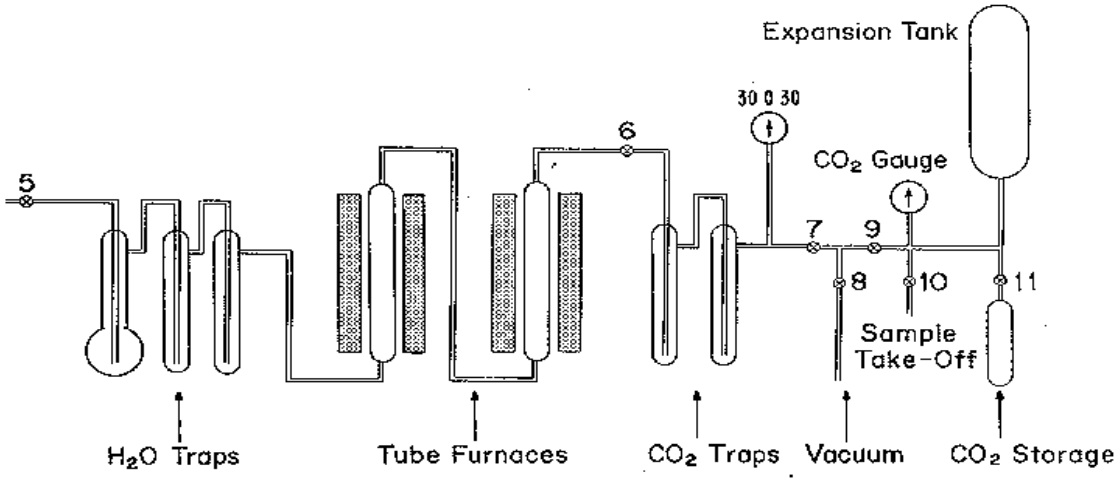

Figure 3. Collection manifold.

Plutonium

Environmental Measurements Laboratory
U. S. Department of Energy

Pu-02-RC

PLUTONIUM IN SOIL SAMPLES

APPLICATION

The plutonium deposited from worldwide fallout and from some nuclear activities can be completely leached with the treatment described. The total dissolution technique may be used for any soil sample.

Plutonium isotopes are leached and equilibrated with ^{236}Pu tracer with HNO_3 and HCl from soil samples up to 1 kg in size. An alternate technique for soil samples of 20 g or less involves total dissolution and equilibration with ^{236}Pu tracer using HNO_3, HCl, and HF. The sample is purified by an ion-exchange method, then electrodeposited on a platinum disc. The plutonium isotopes are measured by α spectrometry.

SPECIAL APPARATUS

1. Double vented conical gravity funnels - i.e., Fisher Scientific - 10-381.

2. Polyethylene dispensing bottle - see Specification 7.11, Vol. I.

SPECIAL REAGENTS

1. Plutonium-236 tracer - a standard solution containing 0.2 Bq g^{-1} in a dispensing bottle. The purity of the tracer is measured by α spectrometry.

2. Standardized 0.1N NaOH.

3. Phenolphthalein indicator - dissolve 500 mg of reagent in 100 mL of 95% ethanol.

DETERMINATION

A. Leach method.

1. Weigh up to 1 kg of prepared soil into an appropriate sized beaker. Add a weighed amount of ^{236}Pu tracer solution (~ 0.05 Bq) from the dispensing bottle.

2. Place a glass stirring rod in the beaker and cover with a watch glass. Immerse the beaker in an ice water bath. **Cautiously** add 900 mL (for a 1 kg sample) or 300 mL (for a 100 g sample) of concentrated HNO_3. Control sample foaming by the addition of from 1-20 drops, as needed, of n-octyl alcohol. When the reaction ceases, **cautiously** add 300 mL (for a 1 kg sample) and 100 mL (for a 100 g sample) of concentrated HCl. **Do Not Stir.** Remove the beaker from the ice water bath, allow the sample to stand at room temperature for 2-4 h, then gradually heat the sample on a low temperature hot plate overnight. The temperature should be high enough so that refluxing occurs and HCl will evaporate out.

3. Allow the mixture to cool and settle, add a sufficient amount of deionized water to provide an 8N HNO_3 solution, then filter through an appropriate sized No. 42 Whatman paper on a Büchner funnel. Wash the residue consecutively with 100 mL of 8N HNO_3. Collect the filtrate and transfer to an appropriate sized beaker (3 L for a 1 kg sample or a 1 L for a 100 g sample).

4. Transfer soil residue and filter back to the original beaker. Add concentrated HNO_3 to completely cover the residue. Allow the mixture to react at low heat on a hot plate for 3-6 h to completely ash the paper and repeat Steps 2 and 3. (If sample is highly organic, Step 2 may have to be repeated a third time.)

5. Evaporate the filtrate from Step 3 to reduce the sample volume.

6. Repeat Steps 2-5 at least twice. The leaching is complete when the soil appears to be white to gray in color. Discard the soil residue (save for **Total Dissolution Method**).

7. Evaporate the combined leachates to about 300 mL; cover with a watch glass and boil to oxidize any remaining organic matter under refluxing conditions.

8. Continue to boil and add concentrated HNO_3 in 10-20 mL increments as needed to maintain the volume at ~ 100-300 mL, to avoid salting out, until all organic material is decomposed. If a precipitate is observed, SiO_2 or TiO_2 is present in the sample. A yellow granular precipitate indicates the presence of TiO_2 and a F^- collection of plutonium has to be performed. For the F^- collection, follow the 12 steps in **Note 1**. A white or gray flocculent indicates the presence of SiO_2, and in this case treatment with HF and HNO_3 is necessary in the following steps.

9. Add an equal volume of water and filter the SiO_2 precipitate through a Whatman No. 42 filter paper by gravity. Wash the precipitate with 1:1 HNO_3, collect the filtrate in a beaker and reserve.

10. Transfer the filter and precipitate to the original beaker and ash the paper with concentrated HNO_3. Then transfer to a platinum dish with 8N HNO_3, add 10 mL of HF and 5-10 mL of $HClO_4$ and place on a low heat hot plate in a hood and evaporate to near dryness.

11. Cool, add 5-20 mL of concentrated HNO_3 and 5-20 mL of concentrated HF to the residue in the platinum dish. Evaporate to near dryness and repeat the addition of acids and evaporations one to three times depending upon the amount of SiO_2 present.

12. Evaporate to dryness slowly. Dissolve the residue with 8N and evaporate to dryness two to four times. Dissolve the SiO_2 with 8N HNO_3 and filter through Whatman No. 42 paper and combine filtrates with filtrates of Step 9. Discard the precipitate.

13. Evaporate the combined solution very carefully at a low heat to about 50-200 mL. Cool to room temperature.

14. Dispense two 100-µL aliquots into 150-mL beakers containing 25 mL of water. Add two to three drops of 0.5% phenolphthalein solution. Titrate the two aliquots with

standardized 0.1N NaOH to the phenolphthalein end point. Calculate the acid normality of the sample solution; adjust to 8N if necessary. Sample is now ready for ion-exchange separation.

B. Total dissolution method.

1. Weigh from 1-20 g of prepared soil into an appropriate sized beaker. Add a weighed amount of ^{236}Pu tracer solution (~ 0.5 Bq) from the dispensing bottle.

2. Place a glass stirring rod in the beaker, cover with a watch glass and immerse the beaker in an ice bath. **Cautiously** add 60-150 mL of concentrated HNO_3. Control sampling foaming by the addition of a few drops of n-octyl alcohol. When the reaction ceases, cautiously add 20-50 mL of concentrated HCl. **Do Not Stir**. Remove the beaker from the ice bath, allow the sample to stand at room temperature for 2-4 h then gradually heat the sample on a low temperature hot plate overnight. The temperature should be high enough so that refluxing occurs, making sure to boil off all traces of HCl.

3. Allow the mixture to cool and settle, then dilute to ~ 8N HNO_3 with water. Filter the soil residue onto a Whatman No. 42 filter paper. Wash the precipitate with 8N HNO_3 making sure all traces of Ca are removed. Collect the filtrate in a 400-mL beaker and reserve.

4. Transfer the filter and soil residue to the original beaker and wet ash with 100-300 mL of concentrated HNO_3. Transfer contents to an appropriate sized platinum dish.

5. Add 5-25 mL of concentrated HF to the soil residue in the platinum dish. Evaporate to dryness at low heat to prevent bumping and repeat the additions of HF and evaporations at least three more times, making sure the residue is reduced to at least a tenth of the original amount.

6. Follow Steps 11-14 of **Leach Method**.

ION EXCHANGE SEPARATION

See Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, Vol. I.

ELECTRODEPOSITION

See Electrodeposition of the Actinides: Mitchell Method, Procedure G-01, Vol. I.

Note 1: <u>Fluoride Collection of Plutonium</u>

1. Cool the solution to room temperature and transfer to a 500-mL Teflon beaker with water.

2. Add 1 g of hydroxylamine hydrochloride and stir until dissolved. Let it stand at room temperature for ~ 10 min.

3. Add 10-mL portions of HF with stirring until all of the TiO_2 precipitate dissolves, then add 10 mL of HF in excess.

4. Add 100 mg of purified Y carrier solution.

5. Allow the F^- precipitate to stand for 1 h.

6. Transfer the precipitate and solution to several 90-mL polyethylene centrifuge tubes and centrifuge for 5 min. Discard the supernate.

7. Stir the precipitate with a plastic stirring rod in each centrifuge tube thoroughly with 10 mL of 1:1 HNO_3 and 10 mL HF, and let stand for about 5 min. Remove the plastic stirring rod and wash with water.

8. Centrifuge for 5 min and discard the supernate.

9. Add 30 mL of saturated boric acid solution, stir, and add 25 mL of HCl to each centrifuge tube. Stir with plastic stirring rod to dissolve.

10. Transfer and combine the solutions from the centrifuge tubes in the original Teflon beaker.

11. Add 1 g of boric acid and evaporate to near dryness. Dissolve with 25 mL of concentrated HCl and 25 mL of concentrated HNO_3. Boil off HCl by two additions of 25 mL of concentrated HNO_3.

12. Evaporate to ~ 25 mL. Cool and dilute with water to 8N HNO_3 and proceed to Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, Vol I.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	$2x10^{-5}$
Yield	(%)	75
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.2

Pu-04-RC

PLUTONIUM IN TISSUE

APPLICATION

This procedure has been applied to the analysis of tissue samples of up to 50 g wet weight. Larger samples should only require adjustment of reagent quantities in the sample preparation.

The tissue sample is wet ashed with HNO_3 and H_2SO_4 and plutonium is collected with $Fe(OH)_2$. Plutonium is then separated by ion exchange and electrodeposited or microprecipitated for α spectrometry.

SPECIAL REAGENTS

1. Ion exchange columns - see Specification 7.5, Vol. I.

2. Double-vented conical gravity funnels (Fisher No. 10-381).

3. Special apparatus for electrodeposition or microprecipitation for α-spectrometry measurement are listed under Procedures G-01 and G-03, Vol. I.

SPECIAL REAGENTS

1. ^{236}Pu tracer, ~ 0.2 g^{-1} - a standard solution is contained in a dispensing bottle. The purity of the tracer is determined by α spectrometry.

2. Iron carrier, 100 mg Fe mL^{-1} - slowly heat 100-g of iron wire in 500-mL of HCl until reaction ceases. Carefully and slowly add 50-mL of HNO_3 while stirring. Cool and dilute to 1 L.

3. Standard 0.1N NaOH.

4. 0.4N HNO_3 - 0.01N HF eluting agent.

5. Anion exchange resin, Bio-Rad AG 1-X4 (100-200 mesh).

6. Methyl red indicator solution - dissolve 100 mg of the dye in 65 mL of C_2H_5OH and dilute to 1 L with water.

7. Phenolphthalein indicator solution - dissolve 100 mg of the dye in 65-mL of C_2H_5OH and dilute to 1 L with water.

SAMPLE PREPARATION

A. Soft tissue.

1. Weigh out the soft tissue samples as received into a 1-L beaker. Add a weighed amount of ^{236}Pu tracer (0.02-0.04 Bq) to each sample from a dispensing bottle.

2. Place a glass stirring rod in the beaker and cover with a watch glass. **Cautiously** add 100 mL of HNO_3 and 100-mL of H_2SO_4. Immediately place the beaker in an ice water bath to control the reaction, then allow the sample to stand at room temperature overnight.

3. Place the beaker on a low temperature hot plate. Completely wet ash the tissue by periodic additions of HNO_3 and gradually increase the hot plate temperature to medium then high until dense SO_3 fumes are evolved. **Note**: This must be done cautiously to avoid bumping. Cool to room temperature.

4. Wash down the sides of the beaker and the cover glass with the minimum amount of water, then heat the sample until dense SO_3 fumes are evolved again. If organic removal is incomplete, add HNO_3 dropwise at a temperature near the point of SO_3 evolution. Cool to room temperature.

5. Add 300 mL of 1:3 HCl, heat the solution to boiling and boil for 10 min. Cool to room temperature. Add 100 mg of Fe carrier solution.

6. Neutralize the solution with NH_4OH and adjust to pH 8. Filter by gravity using double vented conical funnels through a 24 cm Whatman No. 41 filter paper. Wash the precipitate with 1:20 NH_4OH solution. Discard the filtrate.

7. Transfer the paper and precipitate to the original beaker. Add 100 mL of HNO_3, cover with a watch cover and heat on a medium temperature hot plate until the filter is decomposed.

8. Add 200 mL of water and repeat Step 6. Transfer the paper and precipitate to the original beaker. Add 200 mL of HNO_3, cover with a watch cover and evaporate to ~ 100 mL. Repeat the addition and evaporation three times.

9. While still hot, immediately add an equivalent volume of water and filter by gravity through a 15-cm Whatman No. 40 filter paper. Wash the precipitate with 1:1 HNO_3 and collect the filtrate in a 1-L beaker and reserve. Transfer the paper to a 100-mL platinum dish, dry at 110°C and ignite at 600°C.

10. Add 25 mL of HNO_3 and 10 mL of HF to the residue in the platinum dish and evaporate to dryness. Repeat the addition and evaporation.

11. Add 25 mL of HNO_3 and 5 mL of $HClO_4$ and evaporate to dryness. Dissolve the residue with 1:1 HNO_3 and combine with the reserved filtrate from Step 9.

12. Evaporate the solution to ~ 100 mL. Cool to room temperature, transfer to a 250-mL graduated cylinder and record the volume.

13. Dispense a 100-μL aliquot into each of two 150-mL beakers containing 25 mL of water. Add two to three drops of 0.5% phenolphthalein end point. Calculate the normality of the sample solution.

14. Transfer the sample from the graduated cylinder to the original beaker. Wash the graduated cylinder with the amount of water necessary to adjust the normality of the sample solution to 8N HNO_3.

B. Bone.

1. Weigh out the bone samples as received into a 1-L beaker. Add a weighed amount of ^{236}Pu tracer (0.02-0.04 Bq per sample).

2. Place a glass stirring rod in the beaker and cover with a watch glass. Add 100 mL of HCl and 25 mL of HNO_3. Allow the sample to stand overnight at room temperature.

3. Place the sample on a medium temperature hot plate, bring to a boil and boil for 5 min. Add 100 mL of water and filter the sample by gravity through a 15-cm Whatman No. 40 filter paper. Wash the filter with ~100 mL of water. Collect the filtrate in a 1-L beaker and reserve.

4. Transfer the filter to a 100-mL platinum dish, dry at 110°C and ignite at 600°C. Reserve the residue in the platinum dish.

5. Add 100 mg of Fe carrier solution to the reserved filtrate. Dilute the water to ~ 500 mL. Continue the procedure as described in Steps 6-14 of **Sample Preparation**.

ION EXCHANGE SEPARATION

See Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, Vol. I.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	$2x10^{-5}$
Yield		75
Blank	(cps)	-
LLD (400 min)	(Bq)	0.0007
LLD (1000 min)	(Bq)	0.0003
LLD (5000 min)	(Bq)	0.0002

Pu-05-RC

PLUTONIUM IN TISSUE - SOLVENT EXTRACTION

APPLICATION

This procedure has been applied to tissue samples (Fisenne and Perry, 1978).

Plutonium in tissue is equilibrated with ^{242}Pu tracer during wet ashing with NO_3 and HF. The plutonium is separated by solvent extraction with Aliquat-336 from an HNO_3 medium. The plutonium is electrodeposited onto a platinum disc and the plutonium isotopes are resolved by solid-state α spectrometry. (**Note**: The isolated plutonium may be prepared for α spectrometry using the Microprecipitation Procedures, G-03, Vol. I).

SPECIAL APPARATUS

See Eletrodeposition of the Actinides: Talvitie Method, Procedure G-02, Vol. I.

SPECIAL REAGENTS

1. ^{242}Pu tracer solution - about 0.1 Bq g^{-1} of solution in a dispensing bottle.

2. Aliquat-336 (methyltricapryl-ammonium chloride) - 3:7 toluene (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273). Wash four times with an equal volume of 2N HNO_3 and once with an equal volume of 1:1 HNO_3. Prepare 100 mL of acid-washed 3:7 Aliquat-336 for each sample.

3. Calcium nitrate solution - dissolve 6 g of $Ca(NO_3)_2$ in 100 mL of 1:1 HNO_3.

4. Sodium hydroxide, 0.1N - dissolve 4 g of NaOH in H_2O and dilute to 1-L. Standardize the solution against potassium acid phthalate.

5. Phenolphthalein - dissolve 500 mg of reagent in 100 mL of 95% ethanol.

6. 1N HCl - 0.01N HF.

7. Thymol blue indicator - dissolve 400 mg of reagent in 100 mL of water.

SAMPLE PREPARATION

1. Weigh the soft tissue samples as received, place in a Pyrex dish and cut into 2.5 cm cubes with a surgical knife. Weigh the bone samples and proceed with Step 2.

2. Place 500 mL of HNO_3 in a 1500-mL beaker containing a Teflon-coated magnetic stirring bar. Add a known amount of ^{242}Pu tracer by weight (1.7-3.3 mBq per sample) from a dispensing bottle.

3. Place the beaker on a low-temperature magnetic stirrer hot plate. Add the cubed tissue one piece at a time. When the entire sample has been added to the beaker, gradually increase the temperature of the hot plate. Continue stirring and complete the wet ashing with small additions of HNO_3. (Hydrogen peroxide may be used to complete the oxidation if necessary).

4. If any insoluble material remains, filter the sample by gravity through Whatman No. 42 filter paper in a conical funnel. Retain the filtrate in a covered 250-mL beaker.

5. Place the filter in a 100-mL platinum dish or Teflon beaker and ash overnight at 500°C.

6. Cool the platinum dish. Add 25 mL of HNO_3 and 10 mL of HF to the residue. Evaporate to dryness on a high temperature hot plate.

7. Add 25 mL of HNO_3 and evaporate to dryness. Repeat the evaporation twice.

8. Dissolve any residue in 1:1 HNO_3 and combine with the filtrate from Step 4. If trace element analyses are required, continue with Step 9. Otherwise, proceed to Step 12.

9. Evaporate the solution to about 50 mL. Cool to room temperature and transfer to a 100-mL volumetric flask. Wash the beaker with water and transfer the washings to the flask. Repeat the washings to bring the volume to 100-mL.

10. Mix the sample and remove 1-mL for trace elements analyses.

11. Transfer the solution from the volumetric flask to a 400-mL beaker. Rinse the flask three times with 25-mL portions of concentrated HNO_3 and add the washings to the beaker.

12. Evaporate the solution to about 100-mL. Add 25 mg of solid $NaNO_2$ and heat to remove excess nitrite. Cool to room temperature in an ice water bath.

13. Transfer a 10-mL aliquot of the sample into a 150-mL beaker containing 25-mL of water. Add two to three drops of 0.5% phelophtalein. Titrate the aliquot with 0.1 NaOH to the pink phenolphthalein endpoint. Calculate the normality of the sample solution.

14. If the normality lies between 8 and 8.7N in HNO_3, proceed directly to the extraction. If the normality is > 8.7, transfer the sample to a 150-mL graduated cylinder and record the volume. Return the sample to the beaker, add an appropriate volume of water to the cylinder to reduce the acid concentration to 8.5N. Transfer the water from the cylinder to the sample beaker and proceed with the extraction.

SOLVENT EXTRACTION SEPARATION

1. Transfer 50 mL of acid-washed Aliquat-336 into each of two 250-mL separatory funnels. Add 5 mL of $Ca(NO_3)_2$ solution to the first separatory funnel.

2. Transfer the sample the first separatory funnel. Wash the beaker with 1:1 HNO_3 and add the washing to the funnel.

3. Shake the separatory funnel for 3 min. Allow the phases to separate and draw off the aqueous phase into the second separatory funnel. Retain the organic phase in the first funnel.

4. Shake the separatory funnel for 3 min. Allow the phases to separate and draw off the aqueous phase into the second separatory funnel. Retain the organic phase in the first funnel.

5. Combine the two organic phases in one of the separatory funnels.

6. Wash the organic phase twice for 3 min with equal volumes of 1:1 HNO_3. Discard the washings.

7. Wash the organic phase twice for 3 min with equal volumes of HCl. Discard the washings.

8. Strip the plutonium by washing the organic phase twice for 3 min with an equal volume of 1N HCl-0.1N HF. Combine the strip solutions in a 400-mL beaker. Discard the organic phase.

9. Evaporate the solution to near dryness.

10. Add 5 mL of HNO_3 and 0.5 mL of H_2SO_4 to the sample.

11. Evaporate to dense fumes of SO_3. Remove any organic material with dropwise additions of HNO_3.

12. Electrodeposition the sample according to Procedure G-02, Vol. I, or microprecipitate the sample according to Procedure G-03, Vol. I.

13. Measure the plutonium isotopes on an α spectrometry system.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	25
Counter Background	(cps)	1.7×10^{-5}
Yield		75
Blank	(cps)	-
LLD (400 min)	(Bq)	0.65
LLD (1000 min)	(Bq)	0.50
LLD (5000 min)	(Bq)	0.17

*Reagent blanks must be analyzed with the sample.

REFERENCES

Fisenne, I. M. and P. Perry.
"The Determination of Plutonium in Tissue by Aliquat-336 Extraction"
Radiochem. Radioanal. Letters, 33, 259-264 (1978)

Talvitie, N. A.
"Radiochemical Determination of Plutonium in Environmental and Biological Samples by Ion Exchange"
Anal. Chem., 43, 1827-1830 (1972)

Pu-06-RC

PLUTONIUM IN URINE

APPLICATION

This procedure has been applied to the analysis of ^{238}Pu and $^{239,240}Pu$ in urine and in large-area fallout collectors.

The plutonium in urine is equilibrated with a calibrated ^{236}Pu or ^{242}Pu tracer solution. The tracer serves as an internal standard, as well as an indicator of the chemical yield of the other plutonium isotopes. The equilibration is accomplished by treatment with hydrogen peroxide and HNO_3, HCl, HF, and H_2SO_4 during wet ashing. The plutonium is separated by a double anion-exchange column technique; first from a HCl medium, and then from a HNO_3 medium. Finally, the plutonium is electroplated onto a platinum disc or microprecipitated and the plutonium isotopes are resolved by a solid-state α spectrometer.

SPECIAL APPARATUS

See Electrodeposition of the Actinides: Talvitie Method, Procedure G-02, Vol. I.

SPECIAL REAGENTS

1. Standardized ^{236}Pu tracer solution - about 0.17 Bq g^{-1} in dispensing bottle.

2. 0.4N HCl - 0.01N HF.

3. 0.4N HNO_3 - 0.01N HF.

4. Methyl red indicator solution - dissolve 100 mg of dye in 65 mL of ethyl alcohol and dilute to 100 mL with H_2O.

5. Freshly prepared 5% $NaNO_2$ solution.

6. Bio-Rad AG 1-X4 (100-200 mesh, Cl^- from) - see Specification 7.4, Vol. I.

7. Bio-Rad AG 1-X4 (100-200 mesh, NO_3 form) - see Specification 7.4, Vol. I. Convert to NO_3 form by washing the resin with 1:1 HNO_3 until the washings show no trace of Cl- when tested with $AgNO_3$.

SAMPLE PREPARATION

1. Transfer a measured amount of urine into a 3-L beaker, rinsing the container and graduate with HNO_3 and H_2O. Add an exactly weighed amount (10-80 mBq) of standardized ^{236}Pu or ^{242}Pu tracer solution.

2. Add 500 mL of HNO_3, 25 mL of HCl, 10 mL of 1:1 H_2SO_4, and a few drops of octyl alcohol and cover. Allow the mixture to react and heat on a magnetic stirrer hot plate to decompose organic matter.

3. Evaporate to a small volume, adding 30% H_2O_2 repeatedly to assist oxidation. Continue to heat until light SO_3 fumes appear or the organic matter begins to char, then cautiously add a few drops of HNO_3 at a time until all organic matter is completely oxidized.

4. Heat to dense SO_3 fumes, cool, and transfer to a 250-mL Teflon beaker with 1:1 HNO_3.

5. Add 50-mL of HF and heat to SO_3 fumes again. Cool and repeat the addition of HF and HNO_3. Heat to SO_3 fumes, cool, and transfer to an 800-mL graduated beaker with 1:1 HNO_3.

6. Heat the solution until salts dissolve. Cool. Add about 1 g hydroxylamine hydrochloride, stir, then add 1:1 NH_4OH to precipitate metallic hydroxides and heat on a hot plate to coagulate the precipitate.

7. Filter by gravity on a Whatman No. 40 filter paper. Wash thoroughly with 1:10 NH_4OH. Discard the filtrate and washings.

8. Transfer the paper and precipitate to the original beaker. Add 200 mL of HNO3 and 5 mL of HCl, and heat until the paper completely oxidizes.

9. Gradually add HCl and evaporate repeatedly to convert to a HCl medium.

10. Heat the HCl solution while covered until constant boiling occurs, assume the constant boiling HCl solution is ~ 6N HCl. Cool and adjust to 8N HCl by adding half the sample volume of concentrated HCl.

DETERMINATION

1. Cool the 8N HCl solution to room temperature, then add 3 mL of conditioned Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form resin, and then wash with 2:1 HCl until all the resin settles (at least 125 mL).

2. Prepare a large ion-exchange column (Specification 7.5, Vol. I) with a glass wool plug, and about 10 mL of the Cl^- form resin, and then wash with 2:1 HCl until all the resin settles (at least 125 mL).

3. Rinse the cover and sides of the beaker with 2:1 HCl. Decant the solution into the anion exchange column, then wash the resin inthe beaker into the column with 2:1 HCl. Wash the beaker and column with at least 250-mL of 2:1 HCl. Discard the effluent and washings.

4. Elute the plutonium from the column into the original beaker with 250-mL of 0.4N HCl - 0.01N HF solution. Discard the resin.

5. Evaporate the eluate to dryness several times with repeated additions of HNO_3.

6. Add 25 mL of 1:1 HNO_3 and 0.25 mL of freshly prepared 5% $NaNO_2$ solution. Heat the solution to boiling, then cool in an ice water bath.

7. Add about 1 mL of the conditioned Bio-Rad 1-X4 (100-200 mesh, NO_3 form) resin in 1:1 HNO_3 to the solution and stir.

8. Prepare a small ion-exchange column (see Specification 7.6, Vol. I) with a glass-wool plug and about 3 mL of NO_3 form resin and wash with 1:1 HNO_3 until the resin settles.

9. Rinse the cover and sides of the beaker with 1:1 HNO_3. Decant the solution into the anion exchange column, then wash the resin in the beaker into the column with 1:1 HNO_3. Wash the beaker and column with at least 50 mL of 1:1 HNO_3. Discard the effluent and washings.

10. Elute the plutonium from the column into a 150-mL beaker with at least 50 mL of 0.4N HNO_3 - 0.01N HF. Discard the resin.

11. Evaporate the eluate to dryness several times with repeated additions of HCl.

12. See Procedures G-02 or G-03, Vol. I, for electrodeposition or microprecipitation for α spectrometry.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	25
Counter Background	(cps)	0.01
Yield	(%)	80
Blank	(cps)	-
LLD (400 min)	(mBq)	0.60
LLD (1000 min)	(mBq)	0.39
LLD (5000 min)	(mBq)	0.17

*Reagent blanks must be analyzed with the samples.

Pu-07-RC

PLUTONIUM IN LARGE URINE SAMPLES

APPLICATION

Urine samples up to 20 L have been processed using this procedure. Reagent blanks must be analyzed along with the samples. This is a modification of the EML procedure for tissue, Procedure Pu-04-RC.

SPECIAL APPARATUS AND REAGENTS

Apparatus and reagents are the same as for Procedure Pu-04-RC.

SAMPLE PREPARATION

1. Collect large urine samples in 20-L plastic carboys, or other plastic containers.

2. Transfer a known amount of ^{236}Pu or ^{242}Pu tracer by weight (~ 10 mBq for each sample) to a 3-L beaker containing 20 mL of 1:1 HNO_3.

3. Measure out 1 L of urine with a graduated cylinder and transfer to the beaker. Rinse the cylinder with 300 mL of HNO_3. Carefully add the HNO_3 to the beaker, rinse the cylinder with a small amount of H_2O, and add to the sample.

4. Place a glass stirring rod in the beaker to prevent bumping and cover.

5. Place the sample on a medium temperature hot plate and wet ash the urine sample. When the volume in the beaker is low enough to accommodate more sample, add an additional liter of urine and 300 mL of HNO_3. Repeat until the entire sample has been wet ashed.

6. At the last stage of wet ashing, salting out occurs. Dissolve the salts by adding 30-100 mL of 30% H_2O_2 and 100-300 mL of HCl and by heating carefully on a low temperature hot plate.

7. Wash down the sides of the beaker and the cover glass with H_2O. Heat the solution to boiling and boil for 10 min. Cool to room temperature. Add 100 mg of Fe carrier solution.

8. Neutralize the solution with NH_4OH and adjust to pH 8. Filter by gravity using double vented conical funnels (e.g., Fisher No. 10- 381) onto a 24 cm Whatman No. 541 filter paper. Wash the precipitate with 5:100 NH_4OH. Discard the filtrate.

9. Return the paper and precipitate to the original beaker. Add HNO_3 to just cover the paper and precipitate.

10. Cover the beaker with a watch glass and heat on a medium temperature hot plate until the filter is decomposed. Evaporate to about 100 mL.

11. Immediately add an equivalent volume of H_2O and filter by gravity over an 18.5 cm Whatman No. 42 filter paper. Wash the precipitate with 1:1 HNO_3. Collect the filtrate in a 1-L beaker and reserve for plutonium determination.

12. Transfer the paper to a 100-mL platinum dish. Dry at 110°C and ignite at 600°C to oxidize all carbonaceous materials.

13. Cool the dish. Add 25 mL of HNO_3 and 10 mL of HF to the residue and evaporate to dryness.

14. Repeat the addition and evaporation.

15. Add 25 mL of HNO_3 and 5 mL of $HClO_4$. Evaporate to dryness. Dissolve the residue in 1:1 HNO_3 and combine with the main solution reserved for plutonium determination.

16. Evaporate the solution to about 100 mL. Cool to room temperature, transfer to a 250-mL graduated cylinder, and record the volume. Reserve the beaker.

17. Dispense two 100-µL aliquots to two 150-mL beakers containing 25 mL of deionized water. Add two to three drops of 0.5% phenolphthalein. Titrate the two aliquots with standardized 0.1N to a phenolphthalein end point. Calculate the acid normality of the sample solution.

18. Transfer the sample from the graduated cylinder to the original beaker reserved in Step 16. Wash the graduated cylinder with the amount of H_2O necessary to adjust the normality of the sample solution to 8N HNO_3.

19. Proceed to Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, (see Vol. I).

Pu-08-RC

PLUTONIUM IN VEGETATION AND TISSUE - NITRIC/HYDROCHLORIC ACID METHOD

APPLICATION

This procedure has been applied to the determination of plutonium isotopes in tissue and vegetation samples.

The sample is slowly ashed in a furnace at 400ºC and then dissolved by the addition of concentrated HNO_3 followed by concentrated HCl. After filtration of the sample, any remaining residue is further decomposed by the addition of HF.

SAMPLE PREPARATION

1. In an appropriate sized Pyrex beaker weigh out 5-50 g of sample.

2. Place the beaker in a muffle furnace at 100ºC for 1 h. Increase the temperature 100ºC each hour until a final temperature of 400ºC is attained. Continue heating the sample overnight at this temperature.

3. Turn off the muffle furnace and allow the sample to cool to room temperature. When cool, remove the sample from the furnace and spike with a known amount (0.04-0.07 Bq) of ^{236}Pu tracer.

4. Add 150 mL of concentrated HNO_3 to the sample slowly, making sure there is no excessive foaming. Have an ice bath prepared to cool the sample in the event of excessive foaming. After addition of HNO_3, allow sample to react at room

temperature for 15 min. Cover with a watch glass. Heat the sample at a low heat on a hot plate for 30 min. Slowly, add 50 mL of concentrated HCl, allow to react for 15 min. Then heat overnight on a hot plate at a low heat.

5. Remove the sample from the hot plate, add 150-200 mL of H_2O. Allow the sample to cool to room temperature.

6. Using a Büchner funnel with a Whatman No. 42 filter paper, filter the sample under reduced pressure. Wash the insolubles with 1:1 HNO_3 and then with H_2O until the residue becomes colorless.

7. Transfer the filtrate to the beaker, cover with a ribbed watch glass and evaporate the solution on a hot plate to ~ 100 mL.

8. Transfer the filter paper containing the residue from the HNO_3/HCl digestion to a platinum dish. Place the platinum dish in a muffle furnace and heat at 100°C, raise the temperature by increments of 100°C every hour until a final temperature of 400°C is reached. Continue heating at this temperature overnight.

9. Turn off the muffle furnace and let the sample cool sufficiently before removing from the furnace.

10. Add 15 mL of 1:1 HNO_3 and 15 mL of concentrated HF. Heat the sample on a hot plate to near dryness.

11. Repeat Step 10 two times.

12. Add 20 mL of 1:1 HNO_3 to the sample and heat on a hot plate at a low setting until near dryness to remove traces of HF.

13. Repeat Step 12 two times.

14. Add 20 mL of 1:1 HNO_3 to the sample.

15. Filter the sample by gravity using a Whatman No. 40 or No. 42 filter paper into a beaker containing the filtrate fraction. Wash well with 1:1 HNO_3 to bring final volume to ~ 150 mL.

16. Proceed to Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, Vol. I.

Pu-09-RC

PLUTONIUM IN VEGETATION AND TISSUE - NITRIC/SULFURIC ACID METHOD

APPLICATION

This procedure may be used as an alternative to the HNO_3/HCl digestion procedure (see Pu-08-RC). The chemical recovery for the preparation of vegetation and tissue samples by the HNO_3/H_2SO_4 digestion procedure are slightly lower than the recoveries when samples are digested with HNO_3 and HCl.

The sample is digested with HNO_3 and H_2SO_4 until the appearance of SO_3 vapors. Plutonium is coprecipitated with ferric hydroxide by the addition of NH_3, which is free of CO_2. The precipitate is dissolved in an HNO_3 solution then reprecipitated with the addition of NH_3. The iron hydroxide is then dissolved in HNO_3 and the sample is ready for ion exchange separation (see Procedure Pu-11-RC, Vol. I).

SPECIAL REAGENTS

Iron carrier solution (10 mg of Fe mL^{-1}) 7.2 g of $Fe(NO_3)_3 \cdot 9\ H_2O$ diluted to 100 mL with a dilute solution of HNO_3.

SAMPLE PREPARATION

1. In a beaker weigh out 5-50 g of sample.

2. Spike the sample with a known amount (0.04-0.07 Bq) of ^{236}Pu tracer.

3. Slowly add 2 mL of concentrated HNO_3 per gram of sample. Have the beaker in an ice bath to slow the reaction, add n-octyl alcohol if excessive foaming occurs.

4. After addition of HNO_3 is complete, slowly add 0.5 mL of concentrated H_2SO_4 per gram of sample.

5. Take the beaker out of the ice bath and allow to warm to room temperature. Cover the beaker with a watch glass and place on a hot plate at medium heating.

6. When the solution turns dark, add 10-20 mL of concentrated HNO_3 (**Note:** It is necessary to always have an excess of HNO_3 to control the rate of the reaction.) Wash the walls of the beaker with water to remove any remaining residue.

7. Boil solution until there are no HNO_3 fumes and the solution remains clear, then evaporate to vapors of SO_3.

8. Dilute the sample with 300-400 mL of water, add Fe carrier solution at an amount equal to 20 mg of Fe per gram of sample.

9. Cool the sample in an ice bath. At first, slowly add concentrated NH_4OH (free of CO_2), continue adding NH_3 until a pH of 8 is attained, stirring the solution while adding the NH_3.

10. Filter the precipitated $Fe(OH)_3$ by gravity filtration through Whatman No. 40 filter paper using a conical funnel. Wash the beaker with a dilute solution of NH_3 to remove any remaining ferric hydroxide and filter the washings.

11. Transfer the filter paper containing the ferric hydroxide to a 400-mL beaker, then add 100 mL of concentrated HNO_3. Cover the beaker with a watch glass and heat until the filter paper decomposes.

12. Evaporate the sample to a small volume. Cool, carefully add 100 mL of H_2O and add a small amount of concentrated HNO_3 to dissolve the Fe. Boil the solution.

13. Repeat Steps 9-11.

14. Add 100 mL of H_2O to the solution, allow to cool to room temperature. Filter the solution by gravity filtration through Whatman No. 40 filter paper into a 400-mL beaker. Wash with 15-20 mL of 1:1 HNO_3 and H_2O. Discard the filtered residue.

15. Cover beaker with a ribbed watch glass and reduce volume to ~ 5 mL, dilute to 100 mL with 1:1 HNO_3.

16. Proceed to Plutonium Purification - Ion Exchange Technique, Procedure Pu-11-RC, Vol. I.

Radium

Environmental Measurements Laboratory
U.S. Department of Energy

Ra-05-RC

RADIUM-224 IN URINE

APPLICATION

This procedure has been applied only to urine samples. The ^{224}Ra content of urine is determined by chemical isolation of ^{212}Pb and radiometric assay of ^{212}Bi and ^{212}Po after equilibration. Lead-210 and the isotopes of radium, thorium, and actinium are collected from untreated urine by coprecipitation with calcium phosphate. Thorium, actinium, and calcium are then removed by coprecipitation of lead with barium nitrate in the presence of lanthanium hold-back carrier. Radium and added barium are removed by selective precipitation of barium chromate in the presence of ethylenediaminetetraacetic acid. Lead in the filtrate is released from the chelate by the addition of nickel and is finally collected as lead chromate.

The lead precipitate is stored to allow the equilibration of ^{212}Bi and ^{212}Po with ^{212}Pb. The resulting α activity is then determined by scintillation counting. Instrument response is converted to the α activity (Bq) by application of corrections for counter efficiency and background, self-absorption and recovery.

The ^{224}Ra activity (Bq) is calculated from the combined α activity of ^{212}Bi and ^{212}Po by application of the Bateman function for the decay of the thorium series.

SPECIAL APPARATUS

1. Teflon filter holder - see Specification 7.8, Vol. I, - or filter funnels and sample mounts - see Specification 7.12, Vol. I.

2. Glass fiber filters - see Specification 7.8, Vol. I.

3. Magnetic stirrers with Teflon - coated magnet bars.

4. Rings and discs.

5. Alpha phosphors - see Specification 7.10, Vol. I.

SPECIAL REAGENTS

1. Lead carrier solution - 7.99 g $Pb(NO_3)_2$ L^{-1} of 1% HCl.

2. Barium carrier solution - 7.58 g $BaC1_2$ L^{-1} of water.

3. Lanthanum carrier solution - 31.2 g $La(NO_3)_3$ L^{-1} of 1% HCl.

4. Sodium chromate solution - 100 g Na_2CrO_4 L^{-1} of water.

5. Nickel chloride solution - 110.0 g $NiCL_2$ L^{-1} of 1% HCl.

6. EDTA solution - 100.0 g (tetrasodium salt) ethylenediaminetetraacetic acid per liter of water.

SAMPLE PREPARATION

1. Transfer a measured volume of urine to a 250-mL centrifuge bottle.

2. Add 2 mL of H_3PO_4. Adjust the pH to 9 with 1:1 NH_4OH. Stir, centrifuge, and discard the supernate.

3. Dissolve the precipitate with 10 mL of HNO_3. Dilute to about 100-mL with water.

4. Add 1 mL of H_3PO_4. Adjust the pH to 9 with 1:1 NH_4OH. Stir, centrifuge, and discard the supernate.

5. Dissolve the precipitate with 10 mL of HNO_3, and transfer to a 100 mL beaker. Evaporate to near dryness. Repeat the evaporation with 10 mL portions of HNO_3 until the solution is clear.

6. Dilute the sample to about 5 mL with water. Add 1 mL each of barium, lead, and lanthanum carrier solutions.

7. Add 50 mL of 90% (fuming) HNO_3. Stir for 20 min, cool, and filter by suction on a glass fiber filter. Discard the filtrate.

8. Dissolve the precipitate from the filter with water. Collect the solution in a 100-mL beaker. Evaporate to about 5 mL.

9. Add 50 mL of 90% HNO_3. Stir for 20 min, cool, and filter by suction on a glass fiber filter. Discard the filtrate.

DETERMINATION

1. Dissolve the precipitate from the filter with water. Collect the solution in a 40 mL centrifuge tube.

2. Add 3 mL of acetic acid. Adjust the pH to 5.5 with NH_4OH. Add 1 mL of sodium chromate solution with stirring. Cool, centrifuge, and discard the supernate.

3. Dissolve the precipitate with 5 mL of 1:11 HC1. Dilute to 20 mL with water. Add 1 mL of EDTA solution and 3 mL of acetic acid.

4. Adjust the pH to 5.5 with 1:1 NH_4OH. Heat in a water bath to 95°C. Add 1 mL of sodium chromate solution with stirring. Cool, centrifuge, and decant the supernate into a 40-mL centrifuge tube. Discard the precipitate.

5. To the supernate, add 1 mL of nickel chloride solution. Heat to 95°C in a water bath with stirring. Cool and filter by suction on a weighed glass fiber filter. Wash with water.

6. Dry the precipitate at 110°C. Weigh and mount with a zinc sulfide phosphor disc. Store for 10 h and α count in a scintillation counter.

DATA PROCESSING AND ANALYSES

The ^{212}Bi + ^{212}Po disintegration rate is obtained from the net counting rate of the lead chromate precipitate through the following calculation:

$$Bq = R_s\ YTE$$

where R_s is the net counting rate of the sample, Y is the chemical recovery factor, T is the precipitate thickness correction, and E is the counter efficiency factor.

The recovery factor, Y, is obtained by weighing the final precipitate and determining from this measurement the loss incurred through the chemical procedures. The calculation of the recovery factor is:

$$Y = \frac{x}{(w - t)\ f}$$

where x is the weight of lead added as carrier; w is the total weight of the final precipitate and filter paper; t is the weight of the filter paper; and f is the gravimetric factor, which equals 0.641 mg lead per mg of lead chromate.

The precipitate thickness correction, T, is used to normalize self-absorption of the ^{212}Bi and ^{212}Po α activities in samples and standards to a common thickness. T is obtained by counting representative α activities within the energy range of 4.8-8.8 MeV through varying sample thicknesses. The correction is taken as the ratio of counting rates at the minimum thickness to other thicknesses over the range of probable sample recoveries. A composite plot of the correction obtained for ^{230}Th, ^{212}Pb, and ^{226}Ra activities through varying thicknesses of their oxalate, chromate and sulfate derivatives, respectively, is illustrated in Procedure Ra-07-RC, Vol. I, Figure 1.

The efficiency factor, E, is determined by α counting a standard derived from a known equilibrated ^{224}Ra activity under sample conditions.

The ^{224}Ra activity (Bq) is obtained from the ^{212}Bi + ^{212}Po activities through the following calculation:

$$(Bq\ ^{224}Ra) = Bq\ (^{212}Bi + ^{212}Po)\ \ C_1 \times C_2/D$$

where C_1 is the theoretical ratio of ^{224}Ra to ^{212}Pb at equilibrium; C_2 is the theoretical ratio of ^{212}Pb and ^{212}Bi to ^{212}Po at equilibrium; and D is the decay factor used to correct for the decay of ^{212}Pb. The Bateman function for the ratio of ^{224}Ra to ^{212}Pb at equilibrium (C_1) reduces to the following:

$$C_1 + \frac{Bq\ ^{224}Ra}{Bq\ ^{212}Pb} = \frac{\lambda Pb - Ra}{\lambda Pb} = 0.878$$

where

$$t_{1/2},\ ^{212}Pb = 10.64\ h$$
$$t_{1/2},\ ^{224}Ra = 87.36\ h$$

Similarly, the ratio of ^{212}Pb to ^{212}Bi, and ^{212}Po (C_2) reduces to 0.905. The decay correction (fraction remaining) is expressed:

$$\text{Decay Correction} = C^{-\lambda\Delta t}$$

where Δt is the interval between the separation of lead from the radium and the final count. Figure 1 illustrates this correction over a period of 40 h.

The attached computational data sheets show a simplified procedure for the routine calculation of ^{224}Ra disintegration rates. Experimental data are tabulated as they are derived and the calculations are performed on a step-by-step basis.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	50
Counter Background	(cps)	1.67×10^{-5}
Yield	(%)	75
Blank	(cps)	1.67×10^{-3}
LLD (400 min)	(mBq)	3
LLD (1000 min)	(mBq)	2

*Reagent blanks must be analyzed with each set of samples.

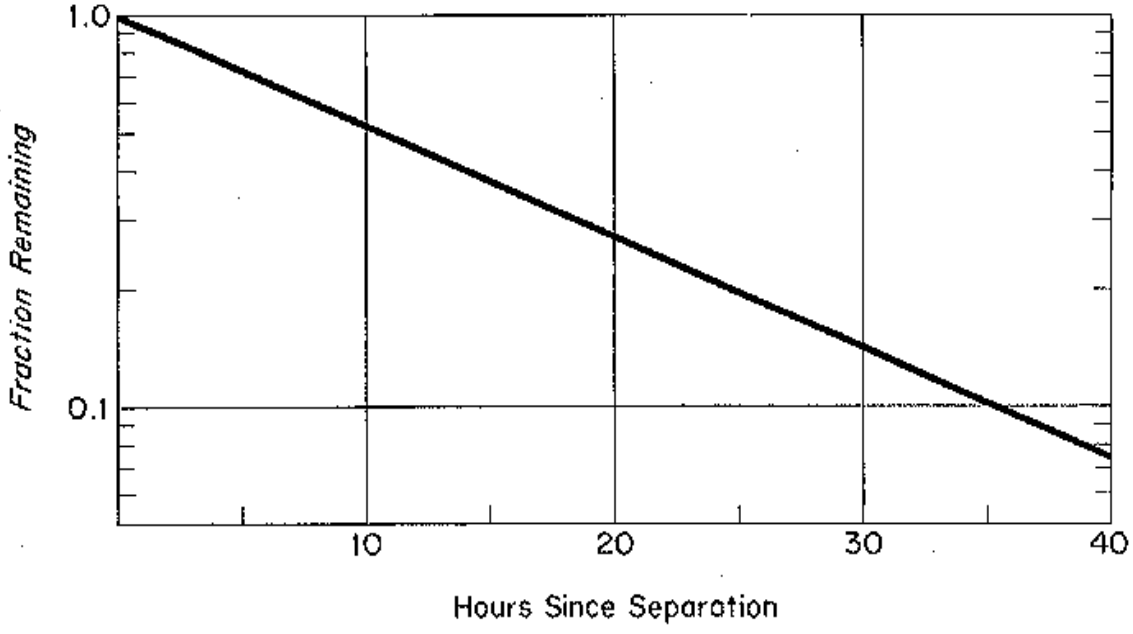

Figure 1. Decay correction.

Date _____ Sample Number

		Operation						
1	Counter number	-						
	STANDARD COUNTING							
2	Gross background count	-						
3	Count time	-						
4	Background (cps)	2/3						
5	Gross standard count	-						
6	Count time	-						
7	Standard (cps)	5/6						
8	Standard (net cps)	7-4						
	CORRECTIONS							
9	Gross weight (mg)	-						
10	Tare weight	-						
11	Net weight	9-10						
12	Weight of lead	11x0.80						
13	Carrier added	-						
14	Chemical yield factor (Y)	13/12						
11	Net weight	Copy						
15	Thickness correction	Graph						

Date _____ Sample Number

		Operation						
16	Counting time (day and h)	-						
17	Separation time (day and h)							
18	Difference (h)	16-17						
19	Decay correction	Graph						
20	Total correction factor	14x15/19						
21	Corrected standard (cps)	8x20						
22	Added (Bq)	-						
23	Efficiency factor (E)	22/21						

Date _____ Sample Number

		Operation						
1	Counter number	-						
4	Background (cps)	Copy						
23	Efficiency factor (E)	Copy						
	SAMPLE COUNTING							
24	Gross sample counts	-						
25	Counting interval (s)	-						
26	Sample (cps)	24/25						
27	Sample (net cps)	26-4						
28	Sample (Bq)	27x23						
	CORRECTIONS							
29	Gross weight (mg)	-						
30	Tare weight	-						
31	Net weight	29-30						
32	Weight of lead	31x0.80						
33	Carrier added	-						
34	Chemical yield factor (Y)	33/32						
31	Net weight	Copy						
35	Thickness correction	Graph						

Date _____ Sample Number

		Operation						
36	Counting time (day and h)	-						
37	Separation time (day and h)	-						
38	Difference (h)	36-37						
39	Decay correction	Graph						
40	Total correction factor	34x35/39						
41	Corrected sample (Bq)	28x40						

Date _____ Sample Number

		Operation						
1	Counter number	-						
3	Count time	Copy						
4	Background (cps)	Copy						
25	Counting interval (s)	Copy						
26	Sample (cps)	Copy						
23	Efficiency factor (E)	Copy						
40	Total correction factor	Copy						
	STANDARD DEVIATON							
42	Background/count time	4/3						
43	Sample/count time (cps)	26/25						
44	S^2	42+43						
45	S for sample (net cps)	$\sqrt{44}$						
46	S for sample (Bq)	45x23x40						

Strontium

Environmental Measurements Laboratory
U.S. Department of Energy

Sr-01-RC

STRONTIUM-89

APPLICATION

This procedure may be used for samples other than soils that can be analyzed by the ^{90}Sr procedure described in Sr-02-RC.

Strontium-89 is ordinarily determined at the same time as ^{90}Sr, thus the radiochemical procedures are those described in Sr-02-RC. The ^{89}Sr content of the sample is calculated by correcting the total counting rate of the $SrCO_3$ fraction for the ^{90}Sr present and for the ^{90}Y, which grows in between separation and counting.

In adapting the ^{90}Sr procedure to include the determination of ^{89}Sr, it is necessary to make two modifications. First, the yield must be determined gravimetrically since ^{85}Sr would interfere in the ß counting of total radiostrontium. This may require a correction for stable Sr which is present in the original sample. Second, the gravimetric procedure requires complete removal of Ca from the Sr fraction.

SPECIAL APPARATUS

The special apparatus are described in Sr-02-RC.

DETERMINATION

1. Transfer the two supernates obtained in **Determination,** Second Milking, Procedure Sr-02-RC, to a 150-mL beaker, heat to boiling, and add 5-10 mL of a saturated sodium carbonate solution slowly with stirring.

2. Cool and filter by suction onto a tared 2.8 cm Whatman No. 42 filter paper. Wash thoroughly with H_2O and alcohol. Record the time of separation of ^{90}Y.

3. Dry, weigh the paper, and precipitate, and then calculate the Sr recovery (**Note:** A 10 mL aliquot of the original Sr carrier solution (20 mg mL^{-1}) is standardized as the carbonate by preparing it for weighing in the same way as described here.)

4. Mount the precipitate on a plastic disc, cover with Mylar film, and fasten with a plastic ring.

5. Beta count the $SrCO_3$ precipitate at 4-day time intervals, recording the measurement times.

6. Beta count the Y oxalate precipitate obtained for ^{90}Sr determination on the same counter at as nearly the same time as possible.

STANDARDIZATION

The best standardization is carried out with a ^{89}Sr standard. Because of the relatively short half-life of this nuclide, however, an indirect standardization may be used. Since the ß energies of ^{89}Sr and ^{40}K are quite close, K salts may be used as the working standards.

A 0.02 g quantity of KCl is mounted with a ring and disc. This is counted at the same time as a precipitated ^{89}Sr standard prepared with 20 mg of Sr carrier as $SrCO_3$. A factor relating the count rates of the two is then determined, so that an apparent ^{89}Sr Bq for the KCl standard is obtained.

$$\text{Apparent Bq } (0.02\,\text{g KCl}) = \frac{\text{Bq } ^{89}\text{Sr std.}}{\text{cps } ^{89}\text{Sr std.}} \times \text{cps KCl}$$

This correction eliminates the difference in self-absorption in the two standards. The error is difficult to reduce by counting smaller aliquots of KCl, since its specific activity is only ~ 15 Bq g^{-1}.

DATA PROCESSING AND ANALYSES

The count rate obtained from the total radiostrontium fraction consists of three components:

1. ^{90}Y (buildup between separation and counting),
2. ^{90}Sr, and
3. ^{89}Sr.

Each of these components has a different ß energy and to a small extent they are affected by differences in self-absorption and are counted with slightly different efficiencies on the same counter. Thus, the correction process for obtaining ^{89}Sr by difference is quite complicated. In this Laboratory, it is simplified by ignoring the small corrections for self-absorption.

The ^{90}Y contribution is determined by calculation. Since the ^{90}Sr content of the sample is known from the original ^{90}Sr determination, the buildup of ^{90}Y between the time of second milking and counting can be computed or may be read off from the graph in Figure 1. The ^{90}Y (Bq) obtained is then converted to ^{90}Y (cps) by using the counter efficiency factor for ^{90}Y.

The ^{90}Sr contribution is determined by counting the corresponding ^{90}Y fraction (from the determination of ^{90}Sr) on the same counter. The ^{90}Y count rate is then corrected for decay to the count rate at the time of the second milking. This ^{90}Y count rate must then be converted to the corresponding count rate for ^{90}Sr. The correction factor is determined experimentally for the individual counter. Measurements are made by separating a ^{90}Sr + ^{90}Y standard of relatively high activity and counting the two fractions as soon as possible. Only slight corrections are then necessary for the buildup and decay of ^{90}Y.

It should be pointed out that all of these computations must be carried out on the count rates at the time of counting the total radiostrontium rather than disintegration rates. The final conversion of the ^{89}Sr (cps) to (Bq) completes the calculation.

The calculation of the standard deviation (SD) due to counting is somewhat more complex than the calculation of the ^{89}Sr disintegration rate. The computational data sheets attached have been prepared as aids in calculating and checking the required values. These sheets cover the gravimetric yield correction applied to the final ^{89}Sr (Bq) calculation, and are also substituted for the ^{85}Sr yield correction shown in the ^{90}Sr (Bq) method, the ^{40}K standardization, the determination of the factor for converting the ^{90}Y count rate to ^{90}Sr count rate, and the final calculation of ^{89}Sr (Bq) (Figure 2).

LOWER LIMIT OF DETECTION (LLD)

		A	B	C	D
Counter Efficiency	(%)	45	45	35	45
Counter Background	(cps)	0.005	0.005	0.005	0.005
Yield	(%)	80	80	80	100
Blank	(cps)	-	-	-	-
LLD (400 min)	(mBq)	10	20	10	5
LLD (1000 min)	(mBq)	5	10	5	3

A = Pure ^{89}Sr
B = ^{89}Sr in a sample containing 1 Bq of ^{90}Sr
C = Pure ^{90}Sr free from ^{90}Y
D = Pure ^{90}Y

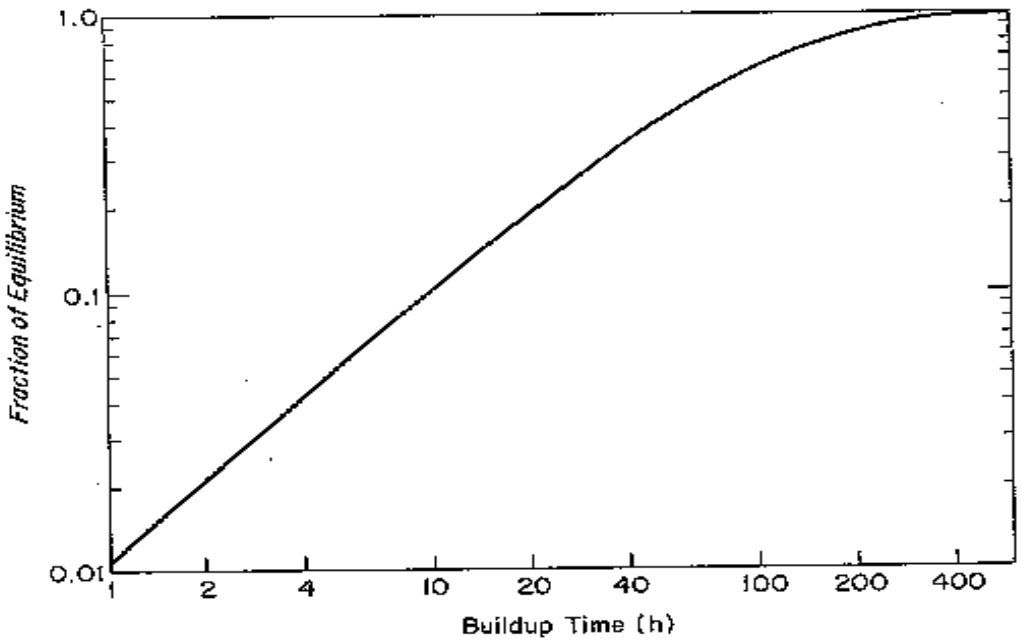

Figure 1. Buildup of ^{90}Y.

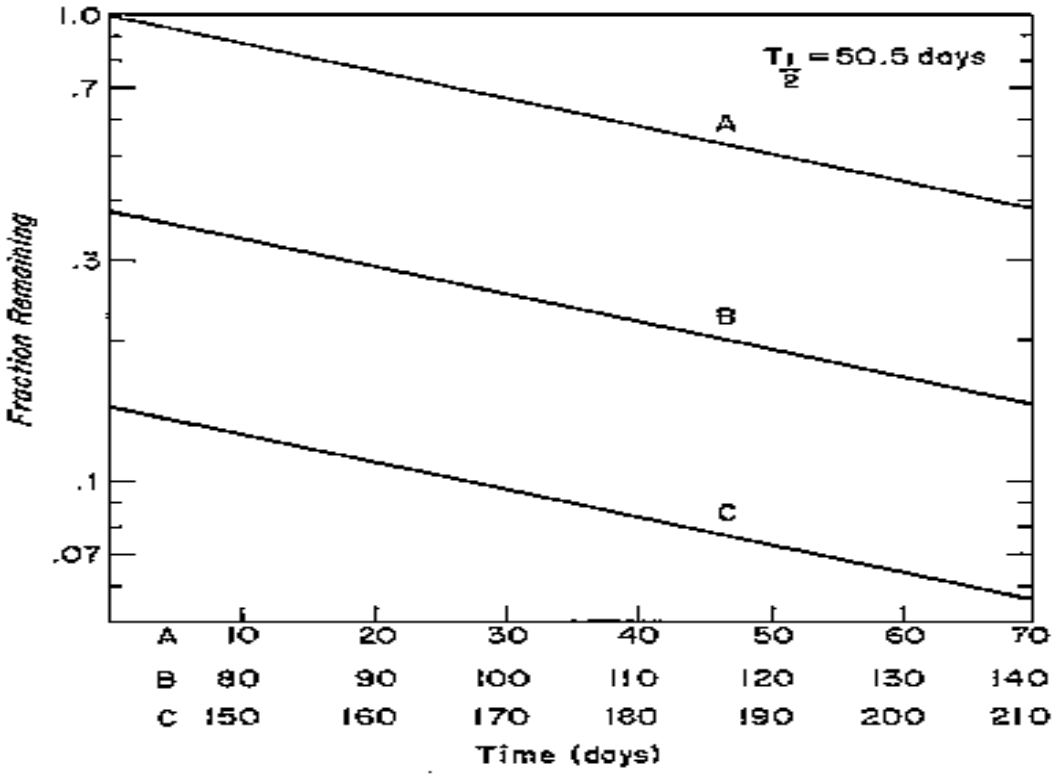

Figure 2. Decay of ^{89}Sr.

Date _____ Sample Number

		Operation						
1	Counter number	-						
4	Background (cps)	Copy						
	^{90}Sr standard counting*							
22	Gross ^{90}Sr count	-						
23	Count time	-						
24	^{90}Sr (cps)	22/23						
25	^{90}Sr (net cps)	24-4						
	CORRECTIONS							
26	Gross weight (mg)	-						
27	Tare weight	-						
28	Net weight	26-27						
29	Weight of Sr	28x0.59						
30	Carrier added	-						
31	Chemical yield factor for Sr	30/29						
32	Corrected ^{90}Sr (net cps)	25x31						
33	Added (Bq)							
34	Efficiency factor (E)	33/32						

*Strontium carbonate counted as soon as possible after ^{90}Y milking.

Date _____ Sample Number

		Operation						
50	Efficiency factor (F)	49/48						
	KCl COUNTING							
51	Gross KCl count	-						
52	Count time	-						
53	KCl (cps)	51/52						
54	KCl (net cps)	53-57						
55	KCl (effective Bq)	54x50						

Date _____ Sample Number

		Operation						
1	Counter number	-						
4	Background (cps)	Copy						
21	Efficiency factor (E)	Copy						
	SAMPLE COUNTING							
56	Gross sample count	-						
57	Count time	-						
58	Sample (cps)	56/57						
59	Sample (net cps)	58-4						
60	Sample (Bq)	59x21						
	CORRECTIONS							
61	Gross weight (mg)	-						
62	Tare weight	-						
63	Net weight	61-62						
64	Weight of Sr	63x0.59						
65	Carrier added	-						
66	Chemical yield for Sr	65/64						
67	Gross weight (mg)	-						
68	Tare weight	-						
69	Net weight	67-68						

Date _____ Sample Number

		Operation						
70	Weight of yttrium	69x0.40						
71	Carrier added	-						
72	Chemical yield for Y	71/70						
73	Time of counting	-						
74	Time of second milking	-						
75	Difference (h)	73-74						
76	Decay correction	Graph*						
77	Total correction factor	66x72/740/376						

**See Sr-02-RC (Vol. II) for ^{90}Y decay curve.

Date _____ Sample Number

		Operation						
1	Counter number	-						
3	Count time	Copy						
4	Background (cps)	Copy						
57	Count time	Copy						
58	Sample (cps)	Copy						
21	Efficiency factor (E)	Copy						
77	Total correction factor	Copy						
60	Sample (Bq)	Copy						
78	Corrected sample (Bq)	Copy						
	STANDARD DEVIATION							
79	Background/count time (cps)	4/3						
80	Sample/count time (cps)	58/57						
81	S^2	79+80						
82	S for sample (net cps)	√81						
83	S for sample (Bq)	82x21x77						

Date _____ Sample Number

		Operation						
1	Counter number	-						
4	Background (cps)	Copy						
55	KCl (effective Bq)	Copy						
	KCl COUNTING							
84	Gross KCl count	-						
85	Count time	-						
86	KCl (cps)	84/85						
87	KCl (net cps)	86-4						
88	Efficiency factor (E)	55/87						
	TOTAL Sr COUNTING	66x72/740/376						
89	Gross total count	-						
90	Count time	-						
91	Total (cps)	89/90						
92	Total (net cps)	91-4						
66	Chemical yield for Sr	Copy						
93	Corrected total (net cps)	92x66						
	^{90}Y SUBTRACTION							
94	Time of counting	-						
74	Time of second milking	Copy						
95	Difference (h)	94-74						

Date _____ Sample Number

		Operation						
96	Buildup factor for ^{90}Y	Graph						
78	Corrected sample (Bq)	Copy						
21	Efficiency factor (E)	Copy						
97	Equilibrium sample (net cps)	78/21						
98	^{90}Y (net cps)	97x96						
99	$^{89}Sr + ^{90}Sr$ (net cps)	93-98						
34	Efficiency factor for ^{90}Sr	Copy						
100	^{90}Sr (net cps)	78/34						
101	^{89}Sr (net cps)	99-100						

Date _____ Sample Number

		Operation						
1	Counter number	-						
101	^{89}Sr (net cps)	Copy						
88	Efficiency factor (E)	Copy						
102	89Sr (Bq)	101x88						
	STANDARD DEVIATION							
81	S^2 for ^{90}Y (total)	Copy						
59	Sample (net cps)	Copy						
98	^{90}Y (net cps)	Copy						
103	S^2 for ^{90}Y (in Sr fraction)	81x98/59						
79	Background/count time (cps)	Copy						
90	Count time	Copy						
91	Total (cps)	Copy						
104	Total/count time (cps)	91/90						
105	S^2 for total (net cps)	79+104						
81	S^2 for ^{90}Sr (net cps)	Copy						
106	S^2 for ^{89}Sr (net cps)	81+103+105						

Date _____ Sample Number

		Operation						
107	S for ^{89}Sr (net cps)	√106						
108	S for ^{89}Sr (Bq)	107x88						
	DECAY CORRECTION							
109	Counting date	-						
110	Sampling date	-						
111	Difference (days)	109-110						
112	Decay correction	Graph						
113	Corrected ^{89}Sr (Bq)	102/112						
114	Corrected S	108/112						

Sr-02-RC

STRONTIUM-90

APPLICATION

Procedures are described for the preparation, separation, and analysis of fallout samples, bone, tissue, milk, urine, vegetation, water and soil. Foods and grains are treated as vegetation.

Strontium is separated from Ca, other fission products and natural radioactive elements. Fuming HNO_3 separations remove the Ca and most of the other interfering ions. Radium, lead and barium are removed with barium chromate. Traces of other fission products are scavenged with yttrium hydroxide. After the ^{90}Sr + ^{90}Y equilibrium has been attained, the ^{90}Y is precipitated as the hydroxide and converted to the oxalate for counting. Chemical yield is usually determined with ^{85}Sr tracer, but instructions for gravimetric yield determination are also included.

SPECIAL APPARATUS

1. Teflon filter holder or filter funnel and sample mount - see Specification 7.12, Vol. I.

2. Rings and discs - see Specification 7.2, Vol. I.

3. Magnetic stirrers with Teflon-coated magnet bars.

4. Mylar film - see Specification 7.3, Vol. I.

5. Glass fiber filters - see Specification 7.8, Vol. I.

6. Fisher filtrator, Fisher Chemical Company.

7. Brinkmann dispenser - pipettor or ordinary pipette.

8. Beta phosphor - see Specification 7.9, Vol. I.

SPECIAL REAGENTS

1. Strontium carrier, 20 mg Sr mL^{-1} - dissolve 48.4 g $Sr(NO_3)_2$ in 1 L of 1:99 HNO_3.

2. Yttrium carrier, 10 mg Y mL^{-1} - see the **Appendix** to this procedure for preparation.

3. Iron carrier, 5 mg Fe mL^{-1} - dissolve 5 g Fe wire in 1:1 HCl and dilute to 1 L with 1:99 HCl, or dissolve 72 g $Fe(NO_3)_3 \cdot 9H_2O$ in 1 L of 1:99 HNO_3.

4. Barium buffer solution - 500 mL 6M acetic acid (glacial HOAC) plus 1 L 6M NH_4OAc plus 0.5 L Ba [$Ba(NO_3)_2$) carrier 10 mg mL^{-1}].

5. Calcium carrier, 200 mg Ca mL^{-1} - dissolve 500 g calcium carbonate ($CaCO_3$) in a minimum of 1:1 HCl and dilute to 1 L with 1:99 HCl.

6. ^{85}Sr tracer, about $7x10^4$ Bq L^{-1} - in a well counter, this tracer provides about 50 counts sec^{-1} mL^{-1}.

7. Sodium carbonate solution, 2M - dissolve 212 g Na_2CO_3 L^{-1} of H_2O.

8. Sodium chromate solution, 0.3M - dissolve 50 g Na_2CrO_4 L^{-1} of H_2O.

9. Sodium hydroxide solution, 6M - dissolve 240 g NaOH L^{-1} of H_2O.

SAMPLE PREPARATION

A. Dry ashing.

Since Sr is not volatile, the majority of samples are prepared by dry ashing. These procedures are described here. Where wet ashing is desirable or preferable, the procedure is given under the analysis of the particular sample type. Freeze-drying is a useful preliminary to many wet-ashing procedures, particularly if it is necessary to take a subsample of the material for the analysis of a volatile element.

Obtaining the required precision and accuracy in radiochemical analyses for natural or fallout radionuclides in materials such as food, vegetation, soils, and water usually requires large samples. Therefore, the ordinary problems of obtaining a suitable ash are magnified. Sample identification, original weight, and ash weight determinations are the same operations as those performed for standard chemical analysis. However, ash weights as taken at EML are not considered as basic data, but are used as an intermediate step in calculating the activity in the original sample. Thus, a completely carbon-free ash is not a necessity.

Dry ashing at EML is conducted as a two-stage process. The first stage is done at about 125°C to completely dry the sample. Subsequently, the temperature is raised at intervals over an 8-h period to 500°C to produce an ash with a small amount of carbon.

The length of time required for drying large samples is 16-24 h. Table 1 lists critical temperatures where ignition will occur. The temperature of the furnace should be raised slowly over a period of 8 h (or more, if necessary) in this critical temperature range. When the upper limit has been reached without sample ignition, the furnace temperature can be raised more rapidly to 500°C and the samples ashed for 16 h.

With the proper adjustment of temperature over the 8-h period, ignition can be avoided on all materials except those containing large amounts of fats such as meat and fish. Although ignition of the sample can be prevented, it is almost impossible to prevent the carbonaceous material from glowing due to oxidation of carbon. The glowing does not interfere with subsequent chemical analyses, except that volatile elements, for example, may be lost since the temperature of the glowing material is considerably higher than the maximum ashing temperature. Therefore, if cesium is to be included in the chemical

analysis, smaller samples ashed at relatively low temperatures should be used in order to minimize the loss of this element. The alternative is to use a wet ashing method.

Different classes of samples require slightly different preparation, however, similar materials may be discussed as a group. In general, food products are prepared as for home use, while other materials are ashed as received. The minimum amounts of raw materials (as determined by this Laboratory) required for a single analytical aliquot are shown in Table 2. Table 3, prepared by the U.S. Federal Food and Drug Administration, gives a more generalized picture of ash percentages and quantities required for specified amounts of Ca.

Edible weights are determined by difference since loss of moisture from the edible portion during the time required for preparation may amount to a sizeable fraction of the mass. Therefore, it is important that the weight of inedible material be determined. There is, of course, some loss of water from the inedible fraction, but this is minimized due to the considerable smaller amount of material involved.

Canned goods are weighed as received and the contents removed. The cans are not washed but are weighed as emptied (including lids), since only the contents removed are the sample. Small amounts of syrup, juices, and solid material sticking to the container are not transferred.

Grains, powdered milk, and macaroni require no preliminary treatment. The sample is placed in stainless steel trays and dried overnight before ashing.

Liquid milk and fruit juices are weighed into deep stainless trays and evaporated at 125°C. The dry material is broken up with a spatula before ashing.

Hay and grass are oven dried below 100°C ground and transferred to stainless trays. The drying is completed at 125°C and the ashing then follows the conditions shown in Table 1.

Fresh vegetables and fruits are prepared as for eating. Thus, green beans are stringed, rinds are removed from oranges and bananas, seeds and rinds are removed from melons, and cores are removed from apples. The outer leaves and central core are removed from the leafy vegetables such as lettuce and cabbage and the heads cut into small pieces before

placing in trays. The refuse is weighed; this weight is deducted from the original weight in order to determine the true sample weight (edible portion).

Root vegetables and potatoes are washed before cutting up into ~ 2.5-cm cubes. Tops are removed and any waste is weighed in order to obtain the edible portion.

Inedible portions of eggs and shellfish are removed and discarded. Thus, eggshells and the shells of the shrimp or clams are removed. The weight of the waste is deducted from the weight of the purchased material to obtain the edible weight.

Three hundred grams of center slices of bread are removed from each loaf, placed in large stainless trays, and dried at 125°C before ashing.

Flour samples are placed in large trays, saturated with distilled water, and kneaded into dough. The samples are then dried in the muffle furnace at 125°C, prior to ashing.

Poultry, meat, fish and similar oily samples are heated in a muffle furnace at 150°C for 1 h. The bones are then easily separated from the soft tissue. The sample is returned to the muffle furnace for drying at 125°C, prior to ashing.

If considerable amounts of carbon remain after 16 h at 500°C, the sample should be crushed, transferred to a smaller metal tray and placed in a muffle furnace regulated at 550°C for 24 h or until ashing is complete. There is always a danger that samples will fuse at this temperature and, therefore, some balance between this problem and the excessive carbon must be reached.

After thorough ashing, the material usually may be removed readily from the tray with a spatula, followed by brushing. A small paint brush is adequate. Except for very small original samples, the weight loss of residual ash in the trays is negligible. Before reuse, the trays are thoroughly scrubbed with detergent and water.

After ashing, all samples should be weighed before further processing. This gives weight of ash per unit weight of original material. The sample must then be ground to pass a 40 mesh screen. Experiments at EML have shown that ash of a coarser size, though blended, may give anomalous analytical results. Since sieving will produce an inhomogenous sample, the ash should be blended thoroughly before analysis. If the entire

ash sample is to be consumed in a single analysis, the grinding and sieving is not necessary.

B. Equipment.

Muffle furnaces in several sizes are used in this Laboratory primarily because of the large variety of samples prepared. A large capacity (1 m^3) muffle furnace which may be operated at 500°C (900°F) continuously is ideal since many different samples or very large samples may be accommodated.

Silica, porcelain, enameled steel, monel metal, stainless steel, and pyrosuran trays have been used. Each type presents its own problems when ashing large samples at 500°C. In all cases, there is deterioration of the tray due to effects of high temperature and of chemical action on the surfaces.

Fused silica trays are useful, but fragile and expensive. After ashing several samples, they tend to become rough from loss of silica by fusion with materials with high alkali salt content such as milk or potatoes. Once these trays are etched, it becomes difficult to completely clean them. Therefore, some ash is lost and a possible source of contamination of future samples is produced. The loss of ash may be unimportant, but the chance of cross-contamination cannot be passed off lightly. Also, the addition of silica to the sample poses a problem in the chemical analysis. Silica trays are of most value when ashing bone, where there is minimal attack on the vessel.

Porcelain trays are similar in behavior to silica. However, they will retain their smooth surface longer than silica trays even though traces of metals fuse into the glaze. Enameled steel is only satisfactory for sample drying, but is easy to clean.

Stainless steel and monel metal trays have proven satisfactory for all ashing operations. They are relatively inexpensive and sturdy. However, if the addition of traces of iron, nickel or chromium to the sample is detrimental to the chemical analyses, these trays should not be used. Cleaning can be accomplished readily with detergents or with dilute mineral acids (usually HCl).

Miscellaneous items that are needed or are useful in the ashing of large samples are several sizes of spatulas, knives, food blenders, food processors, mortars and pestles, ash blenders (preferably of the Patterson-Kelly V type), and sieves.

All large capacity furnaces used in ashing operations should be fitted with fire retardant screens and should exhaust to the laboratory vent system since, during the early part of the ashing, considerable quantities of volatile compounds with low flash points are evolved. These compounds tend to condense in the stack close to the furnace and present a serious fire hazard. The large capacity furnaces should not have forced draft attachments. The forced draft will tend to disturb the ash with a consequent loss of material and possible cross-contamination from one sample to another.

TABLE 1

PRELIMINARY ASHING TEMPERATURES

Material	Temperature (°C)
Eggs	150 - 250°
Meat	Burning
Fish	Burning
Fruit (fresh)	175 - 325°
Fruit (canned)	175 - 325°
Milk (dry)	-
Milk (wet)	175 - 325°
Buttermilk (dry)	-
Vegetables (fresh)	175 - 225°
Vegetables (canned)	175 - 250°
Root vegetables	200 - 325°
Grass	225 - 250°
Flour	Burning
Dry beans	175 - 250°
Fruit juices	175 - 225°
Grains	225 - 325°
Macaroni	225 - 325°
Bread	225 - 325°

TABLE 2

KILOGRAM OF MATERIAL REQUIRED FOR 10 g OF ASH

Item	% Ash*	kg Original Material
Beans (dry)	3.8	0.3
Bread (white)	2.0	0.5
Bread (whole wheat)	2.4	0.4
Eggs (shelled)	0.94	1.1
Fish	1.2	0.8
Flour	0.52	1.9
Fruit (canned)	0.30	3.3
Fruit (fresh)	0.68	1.5
Juices (fruit)	0.59	1.7
Macaroni	0.67	1.5
Meat	0.94	1.1
Milk (buttermilk powder)	11	0.1
Milk (liquid)	0.7	1.4
Milk (powder)	6	0.2
Potatoes	1.1	0.9
Poultry	0.75	1.3
Rice	0.62	1.6
Shellfish	1.8	0.6
Vegetables (canned)	1.1	0.9
Vegetables (fresh)	0.77	1.3
Vegetables (root)	0.72	1.4
Vegetation (hay)	2.3	0.4
Wheat	1.7	0.6

* Mean for 1963-1982

Note: Percent ash is an average value found in routine work. Variations have been found as large as 25% depending upon particular sample composition and ashing conditions.

TABLE 3

SAMPLE SIZE AND ASH WEIGHT FOR ^{90}Sr ANALYSES

	Average Composition			Amount to yield 1 g Ca	
Product	Water (%)	Ash (%)	Calcium (mg 100 g^{-1})	Total wt. of product (g)	Ash wt. (g)
Apples, raw	84.1	0.3	6	16700	50
Applesauce, sweetened	79.8	0.2	4	25000	50
Apricots, dried	24.	3.5	86	1160	40.6
Asparagus, frozen and fresh	93.0	0.7	21	4760	33.4
Beans, snap frozen and fresh	88.9	0.8	65	1540	12.3
Beets, raw peeled	87.6	1.1	27	3700	41.0
Broccoli, raw	89.9	1.1	130	770	8.5
frozen	92.2	0.8	100	1000	8.0
Cabbage, raw	92.4	0.8	46	2170	17.4
Carrots, raw	88.2	1.0	39	2560	25.6
Cauliflower, frozen and fresh	91.7	0.8	22	4550	36.4
Celery, raw	93.7	1.1	50	2000	22.0
Cheese, cheddar	37	3.7	725	138	5.1
Cherries, red, canned, filled	86.6	0.4	11	9100	36.4
Clams, canned	86.7	2.3	87	1150	26.4
Cod, raw	82.6	1.2	10	10000	120
Collards, raw	86.6	1.7	249	400	6.8
Corn, raw	73.9	0.7	9	11100	78
canned	80.5	0.9	4	25000	225
frozen	78.0	0.6	8	12500	75
Crabs, raw	80.0	1.7	(39)	2560	43.5
canned	77.2	1.7	45	2220	37.8
Dates, fresh and dried	20	1.8	72	1390	25.0
Eggs, dried, whole	5.0	3.6	190	526	18.9

TABLE 3 (Cont'd)

Product	Average Composition: Water (%)	Ash (%)	Calcium (mg 100 g^{-1})	Amount to yield 1 g Ca: Total wt. of product (g)	Ash wt. (g)
Figs, dried	24	2.4	186	538	12.9
Grapes, raw	81.9	0.4	17	5900	23.5
Halibut, raw	75.4	1.0	13	7700	77.0
Kale, raw	86.6	1.7	225	445	7.5
Lettuce, head	94.8	0.9	22	4550	41.0
Lobster, canned	77	2.7	65	1540	41.5
Mackerel, canned,					
Pacific	66.0	2.5	260	38	59.6
Atlantic	66.4	3.2	185	540	17.3
Milk,					
whole	87.0	0.7	118	850	5.9
evaporated	73.7	1.5	243	411	6.2
dried (non-fat)	3.5	7.9	1300	77	6.1
Oysters, raw	80.5	2.0	94	1065	21.3
Peaches,					
raw	86.9	0.5	8	12500	62.4
syrup, canned	80.9	0.3	5	20000	60.0
Peanuts,					
roasted, shelled	2.6	2.7	74	1350	36.5
Pears,					
raw	82.7	0.4	13	7700	30.8
syrup, canned	81.1	0.2	8	12500	25.0
Peas,					
raw	74.3	0.9	22	4550	41.0
canned	82.3	1.0	25	4000	40.0
frozen	80.3	0.8	17	5880	47.0
Pineapple, canned	78.0	0.4	29	3450	13.7
Plums, canned	78.6	0.5	8	12500	62.4
Potatoes, raw	77.8	1.0	11	9100	91.0
Prunes, dried	24.0	2.1	54	1850	38.8
Raisins, dried	24.0	2.0	78	1280	25.6
Rice, milled, raw	12.3	0.4	24	4160	16.6
Salmon, raw,					

TABLE 3 (Cont'd)

Product	Average Composition: Water (%)	Ash (%)	Calcium (mg 100 g^{-1})	Amount to yield 1 g Ca: Total wt. of product (g)	Ash wt. (g)
Pacific	63.4	1.0	-	-	-
canned, King (bones)	64.7	2.4	154	650	15.5
canned, Red (bones)	67.2	3.0	259	385	11.6
Sardines, in oil,					
Atlantic	47.1	3.9	354	282	10.9
Pilchards, Pacific	65.2	2.9	(381)	262	7.6
Shrimp, canned					
drained	66.2	5.8	115	870	50.4
Soybeans,					
dried, whole	7.5	4.7	227	440	20.6
Spinach,					
fresh and frozen	92.7	1.5	81	1240	18.5
Squash,					
fresh and frozen	95	0.4	15	6700	26.7
Strawberries, fresh	89.9	0.5	28	3600	18.0
Sweet Potatoes, raw	68.5	1.1	30	3330	36.7
Swordfish, raw	75.8	1.3	19	5260	68.4
Tomatoes, canned	94.2	0.7	(11)	9100	63.6
Tuna fish, canned	52.5	2.3	7	14300	330
Walnuts	3.3	1.7	83	1200	20.5
Wheat, whole grain	13.0	1.7	36	2780	47.3
Flour,					
80% extract	12	0.65	24	4170	27.1
all purpose	12	0.43	16	6250	26.8

SEPARATIONS

A. General.

After ashing, grinding and blending, a suitable aliquot of the ash is taken for analysis. Different sample types are subjected to preliminary separations to bring them to a common point for determination.

B. Bone.

1. Weigh 10 g of bone ash and transfer to an 800-mL beaker. Add 1 mL of Sr carrier solution, 1 mL of ^{85}Sr tracer solution, and 75-100 mL of 1:1 HNO_3 to the sample.

2. Digest the sample on a hot plate for 30 min with occasional stirring. Complete solubilization should be obtained except for traces of carbon and silica.

3. Suction filter the sample into a 250-mL filter flask using a Büchner funnel with a double 7-cm diameter glass fiber filter. Police and wash the beaker with 1:1 HNO_3. Pour the washings through the filters. Wash the residual traces of carbon and silica on the filters with 1:1 HNO_3, followed by a H_2O wash. Discard the filters and residue.

4. Place a magnetic stirrer bar in the original 800-mL beaker. Transfer the filtered sample solution to the beaker. Rinse the filter flask with H_2O and add the rinsings to the beaker.

5. Dilute the sample solution to 500 mL with H_2O. Place the beaker on stirrer/hot plate. Stir and heat the solution to just below boiling.

6. Add 2-3 mL of H_3PO_4 to the heated sample solution while continuing to stir.

7. Adjust the pH of the solution to 4-5 by slowly adding NaOH pellets while stirring. Adjust the pH to 10 by adding NaOH solution (240 g NaOH L^{-1}) to precipitate phosphates. Stir for 30 min.

8. Remove the beaker from the stirrer/hot plate. Allow the phosphate precipitate to cool and settle overnight.

9. Suction filter the sample into a 1-L filter flask through a Büchner funnel with a15-cm diameter glass fiber filter backed with a Whatman No. 42 filter paper.

10. Remove the funnel from the flask and set aside. Test the filtrate for excess phosphate by adding a few drops of $BaCl_2$ solution (15.2 g $BaCl_2$ L^{-1} of H_2O). If no precipitate is observed, insufficient phosphate is present for complete precipitation. In that case, transfer the filtrate to the original 800-mL beaker, add 2 mL of H_3PO_4 to the solution and repeat Steps 7-9, filtering through the filters reserved in Step 9.

11. Discard the filtrate. Rinse the filter flask with H_2O and discard the rinsings.

12. Replace the Büchner funnel containing the phosphate precipitate on the filter flask. Without suction, slowly add 150 mL of hot 1:1 HNO_3 to the Büchner funnel to dissolve the phosphate precipitate.

13. Apply suction and wash the filters with 1:1 HNO_3. Discard the filters.

14. Transfer the solution to the original 800-mL beaker containing the magnetic stirrer bar. Rinse the filter flask with 1:1 HNO_3 and add the rinsings to the beaker. Place the beaker on a hot plate and evaporate the solution to dryness.

15. Cool the beaker and add 60 mL of H_2O. Place the beaker on the stirrer/hot plate. Add 25 mL of 90% fuming HNO_3 to dissolve any solid material. Stir and warm the solution. While continuing to stir, slowly add an additional 195 mL of 90% fuming HNO_3 to the sample. [**Note:** Do this in a well-ventilated hood.] Continue to heat and stir for 30 min.

16. Complete the analysis as described under **Determination.**

C. Ion exchange resin (monthly collection).

1. Transfer the resin and paper pulp to a 150-mL platinum crucible. Dry the contents of the crucible under a heat lamp. Place the crucible in a 500-550^{o}C muffle furnace and ash overnight. Analyze a blank from the same batch of ion exchange resin with each group of samples.

2. Remove the crucible from the furnace and cool to room temperature.

3. Add four times the ash volume (visually determined) of Na_2CO_3 to the crucible and mix thoroughly with the ash.

4. Fuse the sample to a clear melt in a 900°C muffle furnace. Remove the crucible from the furnace and cool to room temperature.

5. Place a Teflon coated magnetic stirrer bar in a 400-mL beaker. Transfer the fused sample to the beaker with 300 mL of H_2O. Place the beaker on a magnetic stirrer/hot plate and stir.

6. Add 1 mL of Sr carrier, 1 mL of Ca carrier, and 1 mL of ^{85}Sr tracer solution to sample. Heat the sample to just below boiling and stir for 1 h.

7. Place a 7-cm glass fiber filter backed with a Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 1-L filter flask.

8. Filter the sample with suction through the funnel. Wash the carbonates retained on the filter with H_2O. Discard the filtrate.

9. Replace the funnel on the filter flask. Dissolve the carbonates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with hot 1:1 HNO_3, followed by H_2O. Discard the filters and any residual material.

10. Transfer the solution with 1:1 HNO_3 washings to the original 400-mL beaker containing a magnetic stirrer bar. Stir and evaporate the solution to dryness.

11. Add 40 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. (**Note:** Do this in a well-ventilated hood.) Stir and slowly add an additional 115 mL of 90% fuming HNO_3 stirring continuously for 30 min.

12. Complete the analysis as described under **Determination**.

D. Milk.

1. Weigh 10 g of milk ash and transfer to an 800-mL beaker. Add 1 mL of Sr carrier solution, 1 mL of ^{85}Sr tracer solution and 100 mL of 1:1 HNO_3 to the sample.

2. Digest the sample on a hot plate for 15-30 min with occasional stirring. Complete solubilization should be obtained except for traces of carbon and silica.

3. Suction filter the sample into a 250-mL filter flask using a Büchner funnel with a double 5.5-cm diameter glass fiber filter. Police and wash the beaker with 1:1 HNO_3. Pour the washings through the filters. Wash the residual traces of carbon and silica on the filters with 1:1 HNO_3. Discard the filters and residue.

4. Place a magnetic stirrer bar in the original 800-mL beaker. Transfer the filtered sample solution to the beaker. Rinse the filter flask with H_2O and add the rinsings to the beaker.

5. Dilute the sample solution to 500 mL with H_2O. Place the beaker on stirrer/hot plate. Stir and heat the solution to just below boiling.

6. Add 2-3 mL of H_3PO_4 to the heated sample solution while continuing to stir.

7. Adjust the pH of the solution to 4-5 by slowly adding NaOH pellets while stirring. Adjust the pH to 10 by adding NaOH solution (240 g NaOH L^{-1}) to precipitate phosphates.

8. Remove the beaker from the stirrer/hot plate. Allow the phosphate precipitate to cool and settle overnight.

9. Suction filter the sample into a 2-L filter flask through a Büchner funnel with a15-cm diameter glass fiber filter backed with a Whatman No. 42 filter paper.

10. Remove the funnel from the flask and set aside. Test the filtrate for excess phosphate by adding a few drops of $BaCl_2$ solution (15.2 g $BaCl_2$ L^{-1}). If no precipitate is

observed, insufficient phosphate is present for complete precipitation. In that case, transfer the filtrate to the original 800-mL beaker, add 2 mL of H_3PO_4 to the solution and repeat Steps 7-9, filtering through the filters reserved above.

11. Discard the filtrate. Rinse the filter flask with H_2O and discard the rinsings.

12. Replace the Büchner funnel containing the phosphate precipitate on the filter flask. Without suction, slowly add 150 mL of hot 1:1 HNO_3 to the Büchner funnel to dissolve the phosphate precipitate.

13. Apply suction and wash the filters with 1:1 HNO_3. Discard the filters.

14. Transfer the solution to the original 800-mL beaker containing the magnetic stirrer bar. Rinse the filter flask with 1:1 HNO_3 and add the rinsings to the beaker. Place the beaker on a hot plate and evaporate the solution to dryness.

15. Cool the beaker and add 60 mL of H_2O. Place the beaker on the stirrer/hot plate. Add 25 mL of 90% fuming HNO_3 to dissolve any solid material. Stir and warm the solution. While continuing to stir, slowly add an additional 195 mL of 90% fuming HNO_3 to the sample. (**Note:** Do this in a well-ventilated hood.) Continue to heat and stir for 30 min.

16. Complete the analysis as described under **Determination**.

E. Rainwater (pot collection).

1. Add 1 mL of HNO_3 L^{-1} of rainwater collected in the stainless steel pot during the sampling period. Add 1 mL of Sr carrier and 1 mL of ^{85}Sr tracer solution to the pot. Evaporate the sample to 100 mL.

2. Transfer the solution to an 800-mL beaker with H_2O. Police the inside of the pot thoroughly with 1:1 HNO_3 and add the washings to the beaker.

3. Evaporate the solution gently to near dryness and transfer the residue to a 150-mL platinum crucible with a minimum of H_2O and 1:1 HNO_3 washes.

4. Evaporate the solution gently to dryness and ash in a 450-500ºC muffle furnace to destroy organic material.

5. Add four times the ash volume (visually determined) of solid Na_2CO_3 to the crucible and mix thoroughly with the ash.

6. Fuse the sample to a clear melt in a 900ºC muffle furnace. Remove the crucible from the furnace and cool to room temperature.

7. Place a Teflon coated magnetic stirrer bar in the original 800-mL beaker. Transfer the fused sample to the beaker with 400 mL of H_2O. Place the beaker on a magnetic stirrer/hot plate. Heat the sample to just below boiling and stir for 1 h.

8. Remove the beaker from the hot plate and cool. Place a 7-cm glass fiber filter backed with a Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 1-L filter flask.

9. Filter the sample with suction through the funnel. Wash the carbonates retained on the filter with H_2O. Discard the filtrate.

10. Replace the funnel on the filter flask. Dissolve the carbonates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with hot 1:1 HNO_3. Discard the filters and any residual material.

11. Transfer the solution with 1:1 HNO_3 washings to the original 800-mL beaker containing a magnetic stirrer bar. Evaporate the solution to dryness.

12. In a well-ventilated hood, add 60 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. Stir and slowly add an additional 195 mL of 90% fuming HNO_3 stirring continuously for 30 min.

13. Complete the analysis as described under **Determination**.

F. Soil (complete solution method).

1. Air dry the entire soil sample and record the weight. Break up the lumps with a wooden roller, sieve through a No. 10 mesh screen. Record the weights of both the fines (soil passing through the sieve) and unsieved soil.

2. Weigh a 100-g representative sample of fines and transfer to a 500-mL platinum crucible. Place the crucible in a 450-500°C muffle furnace overnight to destroy organic matter. Remove the crucible from the furnace and cool to room temperature.

3. Add 400 g of Na_2CO_3 to the crucible and mix thoroughly with the soil. Fuse the sample at 900°C in a muffle furnace until a clear melt is obtained. Remove the crucible from the furnace and cool to room temperature.

4. Tap the bottom of the crucible with a mallet and allow the fused mass to fall into a large mortar. Break up the fused mass with a pestle and grind it to a fine powder.

5. Place a Teflon coated magnetic stirrer bar in a 3-L beaker. Transfer the ground, fused soil sample to the beaker. Wash the mortar and pestle with 200 mL of hot water and transfer the washes to the beaker.

6. Add 10 mL of Sr carrier solution and 1 mL of ^{85}Sr tracer solution to the beaker. Place the beaker on a stirrer/hot plate.

7. Slowly, with continuous stirring, add 1 L of HCl. Heat and evaporate with stirring to a paste.

8. Add 2.5 L of H_2O to the beaker and stir. Remove the beaker from the hot plate and allow the silica to settle.

9. Place a double 24-cm glass fiber filter backed with a Whatman No. 42 filter into a Büchner funnel. Mount the funnel in a 4-L filter flask.

10. Filter the sample with suction through the funnel. Wash the filters with 200-300 mL of hot 1:1 HNO_3, followed by 250 mL of H_2O. Turn off the vacuum, remove the filters from the funnel, and discard.

11. Transfer the filtrate to a 4-L beaker containing a magnetic stirrer bar. Wash the filter flask with H_2O and transfer the washings to the beaker.

12. Place the beaker on the stirrer/hot plate. Stir and warm the solution.

13. Add 50 g of $H_2C_2O_4$ (oxalic acid) to the sample and continue to stir until the salt completely dissolves.

14. While stirring adjust the pH to 5.5-6.0 with NH_4OH. If the brown color of FeO(OH) persists, add additional $H_2C_2O_4$ and readjust the pH. (The optimum condition for the precipitation is an excess of $H_2C_2O_4$ in solution insufficient to cause crystallization of $(NH_4)_2C_2O_4$ upon cooling.)

15. Remove the beaker from the hot plate and allow to stand at room temperature for several hours or overnight.

16. Place a 15-cm Whatman No. 42 filter paper in a Büchner funnel. Mount the funnel in a 3-L filter flask.

17. Stir the sample manually and filter with suction into the flask. Wash and police the beaker with a 10% $H_2C_2O_4$ solution and pour through the filter.

18. Turn off the vacuum and transfer the filter paper and precipitate to a 150-mL platinum dish. Place the dish in a 110°C oven to dry the filter and precipitate. Discard the filtrate.

19. Place the platinum dish in a 450-500°C muffle furnace for 2 h. Raise the temperature slowly to 700°C and continue the ashing for 2 h.

20. Remove the platinum dish from the furnace and cool to room temperature. Transfer the residue to a 250-mL beaker. Rinse the dish with 1:1 HNO_3 and add the rinsings to the beaker.

21. Dissolve the residue in a minimum of 1:1 HNO_3. Add six drops of H_2O_2 to the beaker to facilitate the dissolution. Place the beaker on a hot plate and gently boil.

22. Remove the beaker from the hot plate and cool to room temperature. If insoluble material is present, suction filter the sample through a double 7-cm glass fiber filter into a 250-mL filter flask.

23. Wash the beaker and filters with a minimum of hot 1:1 HNO_3, followed by H_2O. Turn off the vacuum and discard the filters.

24. Return the filtrate to the 250-mL beaker. Rinse the filter flask with H_2O and add the rinsings to the beaker. Gently evaporate the sample to dryness.

25. Dissolve the residual salt in H_2O and perform successive fuming HNO_3 separations, the first two separations at concentrations of slightly > 75%, until the Sr is separated from the bulk of the Ca. Soils with a high Ca content will require five or six additional fuming HNO_3 separations. (The volumes of the 75% HNO_3 solutions may be changed as required by the mass of Ca present, bearing in mind that minimum volumes are desirable.)

26. Complete the analysis as described under **Determination**.

G. Soil (HCl leach method).

1. Air dry the entire soil sample and record the weight. Break up the lumps with a wooden roller and sieve through a No. 10 mesh screen. Record the weights of both the fines (soil passing through the sieve) and the unsieved soil.

2. Weigh a 500-g representative sample of fines and transfer to a 3-L beaker containing a Teflon coated magnetic stirrer bar (see **Note**). Add 10 mL of Sr carrier solution and 1 mL of ^{85}Sr tracer solution to the beaker. Place the beaker on a stirrer/hot plate.

3. Slowly, with continuous stirring, add 1 L of 1:1 HCl. (It may be necessary to add a few drops of $CH_3(CH_2)_6CH_2OH$ [octyl alcohol] to control excessive frothing.) Continue stirring for 30 min. Remove the beaker from the stirrer/hot plate and allow the insoluble material to settle for at least 2 h.

4. Add 2.5 L of H_2O to the beaker and stir. Remove the beaker from the hot plate and allow the silica to settle.

5. Place a double 24-cm glass fiber filter backed with a Whatman No. 42 filter into a Büchner funnel. Mount the funnel in a 4-L filter flask.

6. Filter the sample with suction through the funnel. Wash the filters with 200-300 mL of hot 1:1 HNO_3, followed by 250 mL of H_2O. Turn off the vacuum, remove the filters from the funnel, and discard.

7. Transfer the filtrate to the original beaker containing the magnetic stirrer bar. Wash the filter flask with H_2O and transfer the washings to the beaker.

8. Place the beaker on the stirrer/hot plate. Stir and warm the solution.

9. Add 50 g of $H_2C_2O_4$ (oxalic acid) to the sample and continue to stir until the salt completely dissolves.

10. While stirring, adjust the pH to 5.5-6.0 with NH_4OH. If the brown color of FeO(OH) persists, add additional $H_2C_2O_4$ and readjust the pH. (The optimum condition for the precipitation is an excess of $H_2C_2O_4$ in solution insufficient to cause crystallization of $(NH_4)2C_2O_4$ upon cooling.)

11. Remove the beaker from the hot plate and allow to stand at room temperature for several hours or overnight.

12. Place a 15-cm Whatman No. 42 filter paper in a Büchner funnel. Mount the funnel in a 3-L filter flask.

13. Stir the sample manually and filter with suction into the flask. Wash and police the beaker with a 10% $H_2C_2O_4$ solution and pour through the filter.

14. Turn off the vacuum and transfer the filter paper and precipitate to a 150-mL platinum dish. Place the dish in a 110°C oven to dry the filter and precipitate. Discard the filtrate.

15. Place the platinum dish in a 450-500°C muffle furance for 2 h. Raise the temperature slowly to 700°C and continue the ashing for 2 h.

16. Remove the platinum dish from the furnace and cool to room temperature. Transfer the residue to a 250-mL beaker. Rinse the dish with 1:1 HNO_3 and add the rinsings to the beaker.

17. Dissolve the residue in a minimum of 1:1 HNO_3. Add six drops of H_2O_2 to the beaker to facilitate the dissolution. Place the beaker on a hot plate and gently boil.

18. Remove the beaker from the hot plate and cool to room temperature. If insoluble material is present, suction filter the sample through a double 7-cm glass fiber filter into a 250-mL filter flask.

19. Wash the beaker and filters with a minimum of 1:1 HNO_3, followed by H_2O. Turn off the vacuum and discard the filters.

20. Return the filtrate to the 250-mL beaker. Rinse the filter with H_2O and add the rinsings to the beaker. Gently evaporate the sample to dryness.

21. Dissolve the residual salt in H_2O and perform successive fuming HNO_3 separations, the first two separations at concentrations of slightly >75%, until the Sr is separated from the bulk of the Ca. Soils with a high Ca content will require five or six additional fuming HNO_3 separations. (The volumes of the 75% HNO_3 solutions may be changed as required by the mass of Ca present, bearing in mind that minimum volumes are desirable.)

22. Complete the analysis as described under **Determination**.

Note:

Comparative analyses of soils at EML showed that the HCl leach method yielded ^{90}Sr values which averaged 91% of those obtained by the complete solution method.

H. Soil (NaOH-HCl method).

1. Air dry the entire soil sample and record the weight. Break up the lumps with a wooden roller, sieve through a No. 10 mesh screen. Record the weights of both the fines (soil passing through the sieve) and unsieved soil.

2. Weigh a 250-g representative sample of fines and transfer to a 3-L beaker containing a Teflon coated magnetic stirrer bar (see **Note**). Add 700 mL of H_2O, 10 mL of Sr carrier solution, and 1 mL of ^{85}Sr tracer solution to the beaker. Place the beaker on a mechanical stirrer.

3. Stir the sample for 10 min. While continuing to stir, add 40 mL of 50% NaOH. (The solution should be 1N with respect to NaOH.)

4. Remove the beaker from the mechanical stirrer and cover with a watch glass. Digest the sample overnight on a 70-80°C hot plate.

5. Remove the beaker from the hot plate and allow to cool. While stirring mechanically, cautiously add 900 mL of HCl to neutralize the NaOH and increase the H^+ concentration to 6N. [An additional 500 mL of HCl should be added when analyzing highly calcareous soils to replace the acid required to decompose the carbonates.] A few drops of $CH_3(CH_2)_6CH_2OH$ (n-octyl alcohol) may be added to the sample to prevent excessive frothing.

6. Digest the sample overnight on a 70-80°C hot plate. Remove the beaker from the hot plate and cool to 40-50°C.

7. Place a 24-cm Whatman No. 42 filter paper in a Büchner funnel. Mount the funnel in a 3-L filter flask.

8. Stir the sample. Suction filter the sample into the flask. Police and wash the beaker with three 300-mL portions of hot 1:1 HCl, followed by two 300-mL portions of hot H_2O. Pour the washes through the funnel.

9. Turn off the vacuum. Remove the filter paper and residue from the funnel and place in a 250-mL platinum crucible. Proceed with **Soil Residue** (HF-HNO_3 - Complete Solution).

10. Transfer the filtrate to a 3-L beaker containing a Teflon coated magnetic stirrer bar. Wash the filter flask with H_2O and transfer the washings to the beaker.

11. Place the beaker on a stirrer/hot plate. Stir and warm the solution. Add HNO_3 very cautiously until the vigorous reaction subsides. A few drops of $CH_3(CH_2)_6CH_2OH$ (n-octyl alcohol) may be added to the sample to prevent excessive frothing. Continue adding HNO_3 to a total of volume of 500 mL.

12. Continue to stir while evaporating the sample to 300 mL. Add 500 mL of H_2O to the sample and stir. Remove the beaker from the stirrer/hot plate and cool to room temperature.

13. Place a double 15-cm glass fiber filter in a Büchner funnel. Mount the funnel on a 1-L filter flask.

14. Suction filter the sample through the Büchner funnel. Wash and police the beaker with 50 mL of hot 1:9 HNO_3. Pour the acid through the funnel. Wash the beaker and filter with H_2O several times.

15. Turn off the suction, remove the funnel from the flask and discard the filters.

16. Transfer the filtrate to a 3-L beaker containing a magnetic stirrer bar. Rinse the filter flask with H_2O and add the rinse to the beaker. Place the beaker on a magnetic stirrer/hot plate and stir while warming the solution.

17. Add 50 g of $H_2C_2O_4$ (oxalic acid) to the sample and continue to stir until the salt completely dissolves.

18. While stirring adjust the pH to 5.5 with NH_4OH. If the brown color of FeO(OH) persists, add additional $H_2C_2O_4$ and readjust the pH. (The optimum condition for the precipitation is an excess of $H_2C_2O_4$ in solution insufficient to cause crystallization of $(NH_4)_2C_2O_4$ upon cooling. In most cases, the sample solutions are bright green with white precipitates visible at pH 5.5.)

19. Add a moderate excess of $H_2C_2O_4$ (50-70 g) and readjust the pH to 5.5 with NH_4OH. Continue to heat and stir the solution for 30 min. Check the pH and adjust to 5.5 with NH_4OH if necessary.

20. Turn off the stirrer, remove the beaker from the hot plate, and allow the precipitate to settle overnight.

21. Slowly agitate the supernatant solution with a stirring rod without disturbing the precipitate at the bottom of the beaker. Add 5 mL of Ca carrier solution (200 mg Ca mL^{-1}) and mix into the supernatant solution without disturbing the precipitate. (The additional Ca gives more complete precipitation of SrC_2O_4, especially in the presence of large amounts of Fe.)

22. Allow the new C_2O_4 precipitate to settle for 10-15 min. Place a 25-cm Whatman No. 42 filter paper in a Büchner and mount the funnel in a 3-L filter flask.

23. Suction filter the sample through the funnel. Wash and police the beaker with H_2O adding the washes to the funnel. Wash the precipitate with H_2O until the filtrate is clear. If excess $(NH_4)_2C_2O_4$ is present, rewash the precipitate with hot water.

24. Turn off the vacuum and transfer the filter paper and precipitate to a 150-mL platinum dish. Place the dish in a 110°C oven to dry the filter and precipitate. Discard the filtrate.

25. Place the platinum dish in a 450-500°C muffle furnace for 2 h. Raise the temperature slowly to 700°C and continue the ashing for 2 h.

26. Remove the platinum dish from the furnace and cool to room temperature. Transfer the residue to a 250-mL beaker. Rinse the dish with 1:1 HNO_3 and add the rinsings to the beaker.

27. Dissolve the residue in a minimum of 1:1 HNO_3. Add six drops of H_2O_2 to the beaker to facilitate the dissolution. Place the beaker on a hot plate and gently boil.

28. Remove the beaker from the hot plate and cool to room temperature. If insoluble material is present, suction filter the sample through a double 11-cm glass fiber filter into a 250-mL filter flask.

29. Wash the beaker and filters with 50 mL of 1:1 HNO_3, followed by 50 mL of H_2O. Turn off the vacuum and discard the filters.

30. Return the filtrate to the 250-mL beaker. Rinse the filter flask with H_2O and add the rinsings to the beaker. Gently evaporate the sample to dryness.

31. Dissolve the residual salt in H_2O and perform successive fuming HNO_3 separations, the first two separations at concentrations of slightly > 75%, until the Sr is separated from the bulk of the Ca. Soils with a high Ca content will require five or six additional fuming HNO_3 separations. (The volumes of the 75% HNO_3 solutions may be changed as required by the mass of Ca present, bearing in mind that minimum volumes are desirable.)

32. Complete the analysis as described under **Determination**.

Note:

This method was developed at the U.S. Department of Agriculture Soil Survey Laboratory, Soil Conservation Service, Beltsville, MD. Comparative soil analyses at EML showed that the ^{85}Sr tracer could be completely equilibrated with ^{90}Sr present in the soils when treated consecutively with NaOH and HCl. The NaOH-HCl method yielded results equal to those obtained with the complete solution method.

I. Soil residue (HF-HNO_3 - complete solution).

1. To the residue in a 250-mL crucible reserved in Step 9 of the **Soil (NaOH-HCl) Method**, add 10 mL of Sr carrier and 5-10 mL of Ca.

2. Dry the contents of the crucible in a 100°C oven. Place the crucible in a 500°C muffle furnace and ash overnight.

3. Remove the crucible from the furnace and cool. Place the crucible on a low temperature hot plate and cautiously add 20-30 mL each of HNO_3 and HF. Evaporate the sample to dryness. Repeat the acid additions several times (see **Note 1**).

4. Transfer the dry residue to a mortar and pestle and grind to a fine powder. Return the residue to the platinum crucible.

5. Add 1 mL of ^{85}Sr tracer solution to the crucible. Dry the contents of the crucible in a 100°C oven.

6. Add Na_2CO_3 equivalent to four times the weight of the residue and mix thoroughly. Place the crucible in a 900°C muffle furnace and fuse to a clear melt.

7. Remove the crucible from the oven and cool. Proceed with Step 4 in the **Soil - Complete Solution Method**, but eliminate further addition of Sr carrier and ^{85}Sr tracer solutions (see **Note 2**).

Notes:

1. Upon initial addition of HNO_3 and HF, strong effervescence will occur. After three or four acid additions, the reaction subsides. Final acid additions may be performed with increased heat (medium hot plate setting). When all reaction has ceased, add only HNO_3 and allow the sample to evaporate to dryness. Repeat the HNO_3 addition twice to remove all traces of HF.

2. Adjust the reagent volumes in Step 5 in **Soil (Complete Solution Method)** to the smaller mass of the fused residue (usually 50-100 g).

J. Tap water (monthly composite).

1. Measure 5 L of tap water and pour into a 20-L stainless steel pot. Add 20 mL of HNO_3 and evaporate slowly. Record all tap water and HNO_3 additions.

2. Add 5-L aliquots of tap water daily and 20 mL of HNO_3 weekly to the pot. After the second week, add 1 mL of Sr carrier and 1 mL of ^{85}Sr tracer solution to the pot. Evaporate successively until a 1-month collection has been obtained (100 L).

3. After the final tap water aliquot has been added, evaporate the solution to 100 mL. Transfer the solution to an 800-mL beaker with H_2O. Police the inside of the pot thoroughly with 1:1 HNO_3 and add the washings to the beaker.

4. Evaporate the solution gently to near dryness and transfer the residue to a 15-mL platinum crucible with a minimum of H_2O and 1:1 HNO_3 washes.

5. Evaporate gently to dryness and ash in a 450-500ºC muffle furnace to destroy organic material.

6. Add four times the ash volume (visually determined) of solid Na_2CO_3 to the crucible and mix thoroughly with the ash.

7. Fuse the sample to a clear melt in a 900ºC muffle furnace. Remove the crucible from the furnace and cool to room temperature.

8. Place a Teflon coated magnetic stirrer bar in an 800-mL beaker. Transfer the fused sample to the beaker with 600 mL of H_2O. Place the beaker on a magnetic stirrer/hot plate. Heat the sample to just below boiling and stir for 1 h.

9. Remove the beaker from the hot plate and cool. Place a 9-cm glass fiber filter backed with a Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 1-L filter flask.

10. Filter the sample with suction through the funnel. Wash the carbonates retained on the filter with H_2O. Discard the filtrate.

11. Replace the funnel on the filter flask. Dissolve the carbonates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with hot 1:1 HNO_3. Discard the filters and any residual material.

12. Transfer the solution with 1:1 HNO_3 washings to the original 800-mL beaker containing a magnetic stirrer bar. Evaporate the solution to dryness.

13. In a well-ventilated hood, add 60 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. Stir and slowly add an additional 195 mL of 90% fuming HNO_3 stirring continuously for 30 min.

14. Complete the analysis as described under **Determination**.

K. Tissue and vegetation (wet ashing).

1. Cut the tissue or vegetation into small pieces (see **Note**).

2. Heat 500 mL of HNO_3 in a 1-L beaker. Add the sample in small portions to the hot acid.

3. When all the sample has been added to the beaker and the reaction has subsided, add 1 mL of Sr carrier and 1 mL of ^{85}Sr tracer solution to the beaker.

4. Evaporate the solution to 50 mL. If the solution is turbid and NO_2 fumes are evolving, repeat the evaporation with additional HNO_3.

5. Complete the wet ashing with dropwise additions of HNO_3 and H_2O_2. Gently evaporate the solution to near dryness on a sand bath.

6. Dissolve any solid material in a minimum of 1:1 HNO_3. Transfer the solution to a 400-mL beaker containing a Teflon coated magnetic stirrer bar. Wash and police the 1-L beaker with H_2O, transfering the washings to the sample beaker. Dilute the sample to 200 mL with additional H_2O.

7. Place the beaker on the magnetic stirrer/hot plate and stir. Adjust the pH to 5-6 with solid NaOH pellets. While continuing to stir, add 2-3 g of solid Na_2CO_3. Heat the sample to just below boiling and stir for 30 min.

8. Remove the sample from the hot plate and allow the precipitate to settle overnight.

9. Place a 15-cm glass fiber filter backed with a Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 1-L filter flask.

10. Filter the sample with suction through the funnel. Wash the carbonates retained on the filter with Na_2CO_3 solution (100 g Na_2CO_3 L^{-1}). Discard the filtrate.

11. Replace the funnel on the filter flask. Dissolve the carbonates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with H_2O. Discard the filters and any residual material.

12. Transfer the solution with 1:1 HNO_3 washings to the original 1-L beaker containing a magnetic stirrer bar. Stir and evaporate the solution to dryness.

13. In a well-ventilated hood, add 40 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. Stir and slowly add an additional 115 mL of 90% fuming HNO_3 stirring continuously for 30 min.

14. Complete the analysis as described under **Determination**.

Note:

Most food samples may be simply leached with 1:1 HNO_3, the leachate filtered and diluted to 500 mL with H_2O. After a carbonate collection, the procedure may be continued with Step 6 above.

L. Tissue and vegetation ash (fusion).

1. Weigh 10 g of ash (see **Note**) and transfer to a 150-mL platinum crucible.

2. Add ~ 40 g of solid Na_2CO_3 to the crucible and mix thoroughly with the ash.

3. Fuse the sample to a clear melt in a 900°C muffle furnace. Remove the crucible from the furnace and cool to room temperature.

4. Place a Teflon coated magnetic stirrer bar in an 800-mL beaker. Transfer the fused sample to the beaker with 500 mL of H_2O. Place the beaker on a magnetic stirrer/hot plate and stir.

5. Add 1 mL of Sr carrier and 1 mL of ^{85}Sr tracer solution to the sample. Heat the sample to just below boiling and stir for 1 h.

6. Place a 9-cm glass fiber filter backed with a Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 1-L filter flask.

7. Filter the sample with suction through the funnel. Wash the carbonates retained on the filter with H_2O. Discard the filtrate.

8. Replace the funnel on the filter flask. Dissolve the carbonates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with hot 1:1 HNO_3. Discard the filters and any residual material.

9. Transfer the solution with 1:1 HNO_3 washings to the original 800-mL beaker containing a magnetic stirrer bar. Stir and evaporate the solution to dryness.

10. In a well-ventilated hood, add 60 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. Stir and slowly add an additional 195 mL of 90% fuming HNO_3 stirring continuously for 30 min.

11. Complete the analysis as described under **Determination**.

Note:

Most food samples may simply be leached with 1:1 HNO_3, the leachate filtered and diluted to 500 mL with H_2O. After a carbonate collection, the procedure may be continued with Step 6 above.

M. Urine.

1. Collect a measured 5-L volume of urine (smaller samples are adequate for suspected occupational exposure) in a flask or bottle containing 50 mL of HNO_3 and 1 mL of Sr carrier. After the collection is completed, add 1 mL of ^{85}Sr tracer to the sample.

2. Shake or stir the urine in the collection container to mix. Transfer a 1500-mL aliquot of urine to a 3-L beaker. Add 750 mL of HNO_3 to the beaker and stir the sample.

3. Heat the sample and evaporate to 100 mL. Continue the addition of urine and HNO_3 in a 2:1 ratio until all the sample has been added to the beaker. Rinse the sample container with HNO_3 and add the rinse to the beaker.

4. Evaporate the sample to a small volume (< 100 mL) and complete the wet ashing of the urine with dropwise additions of H_2O_2.

5. Place a Teflon coated magnetic stirrer bar in a 2-L beaker. Transfer the urine sample from the 3-L beaker to the 2-L beaker. Wash and police the 3-L beaker with H_2O, adding the washes to the sample.

6. Dilute the sample to 1 L with H_2O. Place the sample beaker on a magnetic stirrer/hot plate. Heat gently and stir for 15 min.

7. Remove the beaker from the hot plate and cool. Place a 7-cm Whatman No. 42 filter paper into a Büchner funnel. Mount the funnel on a 2-L filter flask.

8. Filter the sample with suction. Wash and police the beaker with 1:1 HNO_3 and add the washings to the funnel. Wash the filter with H_2O.

9. Turn off the vacuum and transfer the filter paper to a 150-mL platinum crucible. Reserve for Step 13.

10. Transfer the filtrate back to the 2-L beaker containing the magnetic stirrer bar. Rinse the filter flask with H_2O and add the rinsings to the beaker.

11. Place the beaker on a magnetic stirrer/hot plate. While stirring, add 203 mL of H_3PO_4 to the sample. Adjust the pH to 5-6 with the addition of solid NaOH pellets. Raise the pH to 10 with the addition of NaOH solution (240 g NaOH L^{-1}).

12. Continue stirring the sample for 30 min. Remove the beaker from the stirrer/hot plate and allow the phosphate precipitate to settle overnight.

13. Dry the reserved filter paper (from Step 9) in a 110°C oven. Place the crucible in a 450-500°C muffle furnace and ash to destroy organic material.

14. Add approximately four times the ash volume (visually determined) of solid Na_2CO_3 to the crucible and mix thoroughly with the ash.

15. Fuse the sample to a clear melt in a 900°C muffle furnace. Remove the crucible from the furnace and cool to room temperature.

16. Place a Teflon coated magnetic stirrer bar in a 400-mL beaker. Transfer the fused sample to the beaker with 200 mL of H_2O. Place the beaker on a magnetic stirrer/hot plate. Heat the sample to just below boiling and stir for 1 h.

17. Filter the two precipitates from Steps 12 and 16 with suction into a 2-L filter flask through the same 15-cm glass fiber filter backed with a Whatman No. 42 filter paper. Remove the funnel from the filter flask and discard the filtrate.

18. Replace the funnel on the filter flask. Dissolve the mixed phosphate-carbonate precipitates on the filter with hot 1:1 HNO_3. Turn on the vacuum and wash the filter with hot 1:1 HNO_3. Discard the filters and any residual material.

19. Transfer the solution with 1:1 HNO_3 washings to the original 800-mL beaker containing a magnetic stirrer bar. Evaporate the solution to dryness.

20. In a well-ventilated hood, add 40 mL of H_2O and 25 mL of 90% fuming HNO_3 to the beaker to dissolve solid matter. Stir and slowly add an additional 115 mL of 90% fuming HNO_3 stirring continuously for 30 min.

21. Complete the analysis as described under **Determination**.

DETERMINATION

A. Final HNO_3 separation.

1. Remove the beaker from the stirrer/hot plate. Cool the beaker and allow the nitrates to settle (see **Note**).

2. Place a 5.5-cm glass fiber filter in a Büchner funnel and mount the funnel in a 1-L filter flask.

3. Suction filter the sample into the flask. Turn off the vacuum, remove the funnel from the flask and set aside.

4. Discard the filtrate and rinse the filter flask with H_2O. Discard the wash.

5. Replace the funnel in the flask. Apply a vacuum while washing the beaker and filter with H_2O to dissolve the precipitate.

6. Turn off the vacuum, remove the funnel and discard the filter.

7. Transfer the solution from the filter flask to a 150-mL beaker with H_2O rinsings. Evaporate the solution slowly to dryness.

8. Place a magnetic stirrer bar in the beaker. Add 23 mL of H_2O to the beaker, stir, and warm to dissolve the residue. Add 77 mL of 90% fuming HNO_3 to the beaker and continue heating and stirring for 30 min.

9. Turn off the stirrer and remove the beaker from the hot plate. Cool the sample, allowing the $Sr(NO_3)_2$ to settle.

10. Suction filter the precipitate through a double 2.8-cm glass fiber filter with a Fisher filtrator and Teflon filter assembly into a 250-mL beaker.

11. Turn off the vacuum and remove the beaker from the filtrator. Discard the filtrate.

12. Place a 40-mL heavy wall conical centrifuge tube in a 250-mL beaker and set inside the filtrator under the filter assembly.

13. Dissolve any remaining precipitate in the sample beaker with a minimum of H_2O. Pour through the funnel, collecting the solution in the centrifuge tube. Wash the filter with H_2O, keeping the volume < 20 mL.

Note:

If the yield is to be determined by the gravimetric method all the Ca must be separated from the Sr. A sufficient number of fuming HNO_3 separations, usually four to five, must be performed to ensure complete Ca separation. Under these conditions Ba and Pb also precipitate but are removed in subsequent OH^{-1} and $CrO4^{-2}$ scavenging steps. If the yield is to be determined by measurement of the ^{85}Sr tracer, a few mg of Ca may remain with the Sr.

B. First milking.

1. Add 1 mL of Fe carrier solution to the separated Sr fraction in the centrifuge tube. Stir the solution and place the tube in a 90°C water bath to warm.

2. While stirring, adjust the pH of the sample to 8 with NH_4OH. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath. Remove and rinse the stirring rod.

3. Centrifuge the sample for 5 min. Decant the supernate into a second 40-mL centrifuge tube. Reserve the supernate for Step 6 and note the hour and date of this initial OH^{-1} precipitation as "First Milk Separation Time."

4. Dissolve the precipitate in the first centrifuge tube in a few drops of HCl and dilute to 5-10 mL with H_2O. Stir the solution and warm the tube in the hot water bath.

5. While stirring, adjust the pH of the sample to 8 with NH_4OH. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath. Remove and rinse the stirring rod with H_2O.

6. Centrifuge the sample for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Discard the residue in the first centrifuge tube. Adjust the volume of the combined supernates to 20 mL with H_2O.

7. While stirring, add 4 mL of Ba buffer solution to the sample. Adjust the pH of the sample to 5.5 with either 1:1 HCl or NH_4OH (see **Note 1**).

8. Return the centrifuge tube to the hot water bath. While stirring, add 1 mL of 0.3M Na_2CrO_4 dropwise to the sample. If necessary, while stirring add additional Na_2CrO_4 solution dropwise to give a strong yellow CrO_4^{-2} color to the solution (see **Note 2**). Allow the sample to digest in the water bath for 10 min.

9. Remove and rinse the stirring rod with H_2O. Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube for 5 min. Decant the supernate into a 30-mL polyethylene bottle. Discard the residue in the centrifuge tube.

11. Add 10-15 drops of HCl and exactly 1 mL of Y carrier solution to the sample in the polyethylene bottle.

12. Store the sample for 2 weeks to allow equilibration of ^{90}Y (see **Note 3**).

Notes:

1. The pH of the solution is critical at this point. Complete precipitation of $BaCrO_4$ will not occur in a more acid solution and Sr will partially precipitate in more basic solutions.

2. If large quantities of Ba are present in the sample; i.e., soils, a partial precipitation as the $BaCrO_4$ may occur. The sample is centrifuged and the supernate decanted into another 40-mL centrifuge tube. The precipitation is completed by the dropwise addition of 0.3M Na_2CrO_4 and the analysis is continued with Step 10.

3. If less than complete buildup of ^{90}Y is acceptable, the "First Milk Separation Time" noted in Step 3 is the start of the build-up period. A correction for ^{90}Y buildup between the first and second milking must be included in the calculation.

C. Strontium-85 yield measurement.

1. Dilute the sample solution from Step 12 of **First Milking** to the bottom of the neck of the polyethylene bottle with H_2O.

2. Measure the activity of the sample with a NaI(Tl) crystal, collecting at least 10^4 counts. Transfer a 1-mL aliquot of the original tracer solution in a 30-mL polyethylene bottle and dilute to the bottom of the bottle neck with 1N HCl. Measure the activity of the tracer solution.

3. Calculate the ^{85}Sr yield of the sample compared with the unprocessed tracer solution.

D. Second milking.

1. Transfer the sample from the polyethylene bottle to a 40-mL, heavy-walled, conical centrifuge tube. Rinse the bottle with a minimum of H_2O and add the rinse to the centrifuge tube. Stir the solution and place the tube in a 90°C water bath to warm.

2. While stirring, adjust the pH of the sample to 8 with NH_4OH. Add six drops of H_2O_2 to the sample and heat for 1 h to remove excess H_2O_2. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath. Remove and rinse the stirring rod.

3. Centrifuge the sample for 5 min. Decant the supernate into a 60-mL polyethylene bottle. Record the hour and date of the precipitation as "Second Milk Separation Time."

4. Dissolve the precipitate in the centrifuge tube with four drops of HCl and stir. Dilute the sample to 15-20 mL with H_2O. Stir the solution and warm the tube in the hot water bath.

5. While stirring, adjust the pH of the sample to 8 with NH_4OH. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath. Remove and rinse the stirring rod with H_2O.

6. Centrifuge the sample for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Reserve the supernates for possible additional milking. (**Note:** Steps 7-10, below, are designed to remove traces of ^{85}Sr from the ^{90}Y fraction. If a gravimetric yield determination is to be made, these steps may be omitted.)

7. Add 25-30 mL of H_2O to the precipitate. Add four drops of HCl to the tube and stir until the precipitate dissolves.

8. Add 20 mg of Sr holdback carrier to the tube and stir. Place the centrifuge tube in the hot water bath. While stirring, adjust the pH to 8 with NH_4OH.

9. Remove and rinse the stirring rod with H_2O. Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube for 5 min. Decant and discard the supernate.

11. Add three drops of HCl to dissolve the precipitate (from Step 6 or Step 10), stir to dissolve, and add 25-30 mL of H_2O.

12. Stir the sample and place the tube in a hot water bath. Add 1 mL of saturated $H_2C_2O_4$ (oxalic acid) dropwise with vigorous stirring.

13. Add two to three drops of NH_4OH with stirring. Continue the dropwise addition of NH_4OH to adjust the pH to 2-3. Digest the sample in the hot water bath for 1 h.

14. Remove the tube from the hot water bath. Rinse and remove the stirring rod from the tube. Cool the tube to room temperature in a cold water bath.

15. Centrifuge the tube for 10 min. Decant and discard most of the supernate.

16. Using a Teflon filter funnel assembly, filter the precipitate by suction through a weighed 2.8-cm Whatman No. 42 filter paper, backed with a 2.8-cm glass fiber filter.

17. With the suction on, remove the filter funnel. Turn off the vacuum and remove the filtered precipitate. Discard the filtrate.

18. Dry the filtered precipitate in a 110°C oven. Weigh the filtered precipitate to determine the gravimetric yield.

19. Mount the filtered precipitate on a nylon disc, place a plastic ß scintillation phosphor directly on the precipitate, cover the phosphor with Mylar, and fasten the assembly with a nylon ring.

20. Store the mounted sample for 3 h prior to measurement to allow the decay of short-lived ^{222}Rn progeny present due to the filtration operation.

21. Measure the sample in a low-level ß scintillation counter, recording the hour and date of the beginning of the measurement period.

22. Calibrate the beta counter with a ^{90}Y standard which has been precipitated and mounted in the identical manner as the sample.

E. Gravimetric Sr yield determination.

1. Transfer the solution from the polyethylene bottle, Step 6 under **Second Milking**, to a 150-mL beaker and gently heat to a boil on a hot plate.

2. With continuous stirring, **cautiously** add 5-10 mL of saturated Na_2CO_3 solution to the sample. Continue to heat gently for 10 min.

3. Remove the beaker from the hot plate and cool to room temperature. Place a preweighed 5.5-cm glass fiber filter in a Büchner funnel mounted in a 250-mL filter flask.

4. Suction filter the precipitate using care to prevent the precipitate from creeping under the filter. This can be accomplished by filtering only through the center area of the filter.

5. Wash the beaker, precipitate, and filter thoroughly with H_2O, followed by C_2H_5OH. Turn off the vacuum and remove the filtered precipitate from the funnel.

6. Dry the filter in a 110°C oven. Weigh the filter.

7. Determine the Sr concentration of the original Sr carrier solution by precipitating $SrCO_3$ from a 10-mL aliquot of the solution as described above.

8. Determine the gravimetric Sr yield of the sample.

F. Gravimetric Y yield measurement.

1. Determine the weight of yttrium oxalate as described in Steps 15-18 of **Second Milking**.

2. Standardize triplicate 10-mL aliquots of the original Y carrier solution each time a fresh batch is made by precipitating the oxalate as described and filtering on a weighed 5.5-cm glass fiber filter.

CALCULATIONS

The ß counting data obtained from the ^{90}Y precipitate must be corrected to give the proper radioactivity rate representing the ^{90}Sr in the sample. The corrections include those for buildup of ^{90}Y, counter background, ^{90}Y efficiency, Sr yield, Y yield, and ^{90}Y decay. As the ^{90}Y beta is very energetic and is always counted with the same weight of precipitate, no correction for self-absorption is necessary.

Ordinarily no correction is made for the degree of buildup of ^{90}Y during the equilibration since a 2-week build-up period gives over 97% of the expected equilibrium value. When shorter build-up periods are used to hasten analysis, however, appropriate correction must be made.

The counter background is determined weekly, but the value used is a running mean for 8 weeks. The efficiency is determined twice a month by counting the ^{90}Y derived from a ^{90}Sr standard of known activity rate. The procedure at EML is to weight 20 mg of $SrCO_3$ prepared with a known specific activity (~ 0.1 Bq mg^{-1}). The $^{90}SrCO_3$ is dissolved in H_2O and HCl and the second milking procedure is carried out. The running mean for 8 weeks is used for the efficiency.

The Sr yield is ordinarily determined by measuring the recovery of ^{85}Sr tracer added to the sample. Since an aliquot of the original ^{85}Sr tracer solution is counted at the same time as the samples, there is no need to know the radioactivity rate of the tracer nor to apply decay corrections.

A correction must be made for the decay of ^{90}Y from the time of the second milking to the time of measurement. This may be done graphically by reading the decay factor from the graph shown in Figure 1.

A sample computational data sheet, which is used for recording and checking calculations, is reproduced on the following pages. The present calculations are handled entirely by computer.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	45
Counter Background	(cps)	0.005
Yield (Sr)	(%)	80
Yield (Y)	(%)	100
Blank	(cps)	
LLD (400 min)	(Bq)	0.007
LLD (1000 min)	(Bq)	0.003

APPENDIX

A. Purification of yttrium carrier.

1. Dissolve 100 g of Y nitrate, $Y(NO_3)_3\ 6H_2O$, in 80 mL of water. Add a few drops of HNO_3. Transfer to a 1-L separatory funnel using two 20-mL portions of H_2O.

2. Add 120 mL of saturated NH_4NO_3 to the separatory funnel. Add 240 mL of tributyl phosphate (TBP) to the separatory funnel and shake for 5 min. Allow the phases to separate for 10 min.

3. Draw off the aqueous (lower layer) into a second separatory funnel. Add 240 mL of fresh TBP and shake for 5 min. Allow the phases to separate and discard the aqueous (lower layer).

4. Combine both TBP phases in one separatory funnel, add 20 mL of H_2O and shake for 5 min. Allow the phases to separate and transfer the aqueous (lower layer) to a clean separatory funnel.

5. Repeat the H_2O wash and combine the aqueous fractions. Discard the TBP.

6. Add 50 mL of CCl_4 to the H_2O solution, shake for 1 min, and allow to separate. Discard the CCl_4.

7. Dilute to 2 L with H_2O and store in polyethylene.

B. Yttrium carrier counting check.

1. Pipette 1 mL of Y carrier into each of three 40-mL centrifuge tubes. Dilute to 20 mL with H_2O.

2. Heat in a water bath to about 90°C. With stirring, adjust the pH to 8 with NH_4OH. Digest for 10 min and cool in a cold water bath.

3. Centrifuge for 5 min. Decant and discard the supernate.

4. Break up the precipitate with a few mL of H_2O. Dilute to 20 mL with H_2O. Add a few drops of concentrated HCl to just dissolve the precipitate. Heat the solution in a water bath to about 90°C and add 1 mL of saturated $H_2C_2O_4$ (oxalic acid) dropwise while stirring.

5. Allow the precipitate to digest for about 1 h. Cool to room temperature and filter on a 2.8-cm Whatman No. 42 filter paper. Discard the filtrate.

6. Dry in a 110°C oven. Mount with a nylon ring and disc with a ß scintillation phosphor and count.

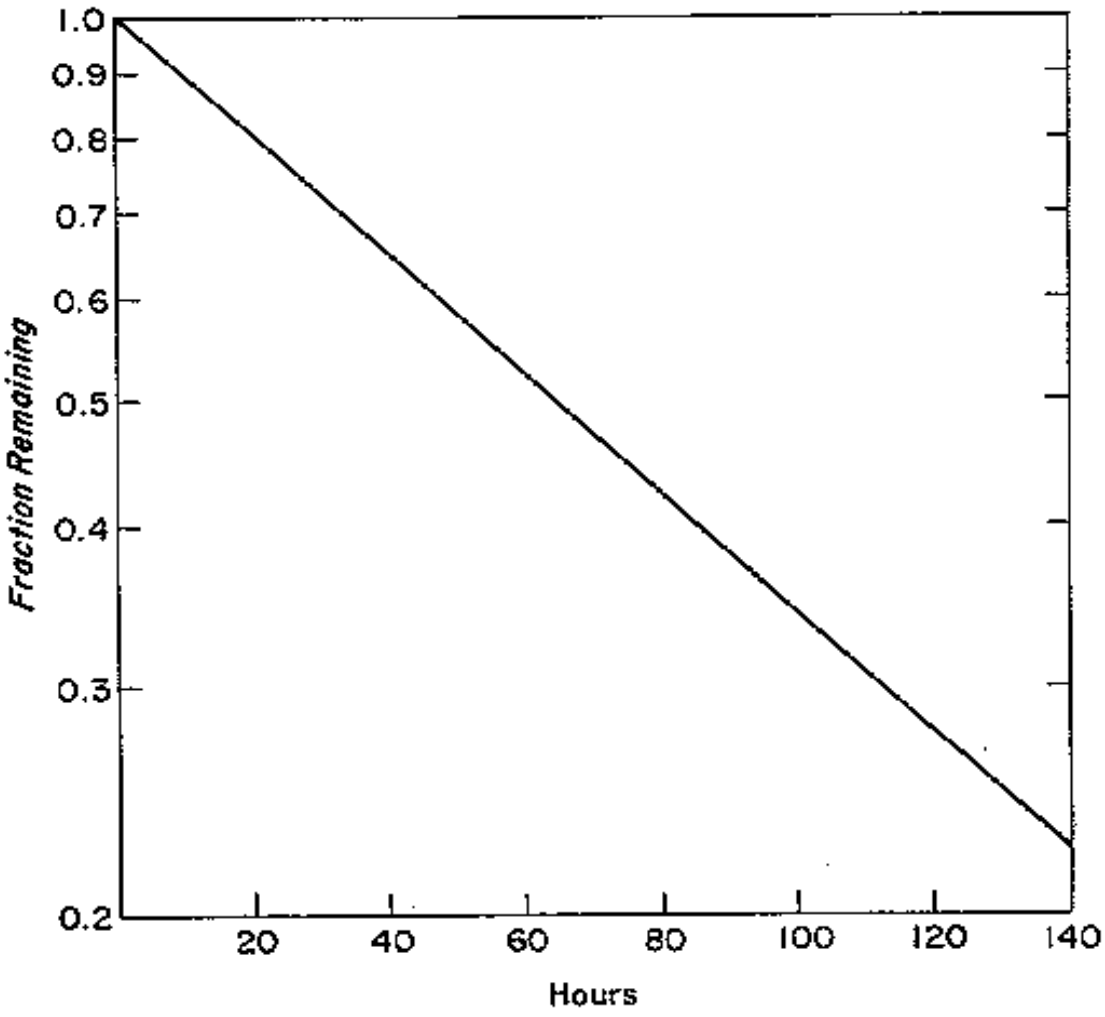

Figure 1. Decay of ^{90}Y (T1/2 = 64.6 h).

Technetium

Environmental Measurements Laboratory
U.S. Department of Energy

Tc-01-RC

TECHNETIUM-99 IN WATER AND VEGETATION

APPLICATION

This procedure has been applied to the analysis of water and vegetation.

Technetium-99 is equilibrated with ^{95m}Tc tracer. The technetium is separated from other elements by anion exchange and electrodeposition. The ^{99}Tc is β counted. Gamma spectroscopy measurement of ^{95m}Tc provides the chemical yield.

SPECIAL APPARATUS

1. Virgin platinum discs - 17.6 mm diameter x 0.127 mm mirror finish on one side.

2. Plating cells - see Specifications 7.15 and 7.16, Vol. I.

3. Electrodeposition power supply - constant, capacity 0-1.5 A, 0-20 V; transistorized variable speed stirring motor.

4. Ion exchange columns - see Specification 7.5, Vol. I.

5. Mylar film - see Specification 7.3, Vol. I.

6. Beta phosphor - see Specification 7.9, Vol. I.

7. Rings and discs - see Specification 7.2, Vol. I.

8. Germanium lithium, Ge(Li), γ-ray spectrometer.

SPECIAL REAGENTS

1. Standardized ^{99}Tc solution - available from NIST.

2. Technetium-95m tracer solution (free from ^{97m}Tc) - prepared by helium nuclei bombardment of pure ^{93}Ni foil in a cyclotron.

3. Methyl red indicator solution - dissolve 100 mg of the dye in 65 mL of ethyl alcohol and dilute to 100 mL with water.

4. Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form) anion exchange resin - see Specification 7.4, Vol. I.

5. 6M sodium hydroxide solution - 240 g NaOH L^{-1} of water.

6. 2M sodium carbonate solution - 212 g $Na_2CO_3 L^{-1}$ of water.

7. Calcium solution - 200 mg Ca mL^{-1} - dissolve 500 g $CaCO_3$ in a minimum of 1:1 HCl and dilute to 1 L with 1:99 HCl.

8. Barium solution - 20 mg Ba mL^{-1} - 30.4 $BaCl_2$ L^{-1} of 1:99 HCl.

9. Iron solution - 5 mg Fe mL^{-} - dissolve 72 g $Fe(NO_3)_3 \cdot 9 H_2O$ in 1 L of 1:99 HNO_3.

10. 5M HNO_3 eluting solution - dilute 325 of mL of HNO_3 to 1L.

11. 0.1M HNO_3 wash solution - dilute 6.5 mL of HNO_3 to 1L.

SAMPLE PREPARATION

A. General.

To a measured quantity of sample in a glass beaker add a known amount of ^{95m}Tc tracer which gives 60 counts sec^{-1} at 204 keV as of count date on a Ge(Li) γ-ray spectrometer.

B. Water.

Evaporate to a small volume. Cool and add about 800 mL of water. Stir and filter with suction through a 15 cm glass fiber filter. Discard the silica and insoluble material.

C. Vegetation.

Wet ash with HNO_3. After wet ashing is completed, evaporate to the smallest volume possible with no salting out. Cool and add about 800 mL of water. Stir and filter with suction through a 15-cm glass fiber filter. Discard the silica and unsoluble material.

SEPARATION

1. Evaporate the filtrate to about 200 mL.

2. Add 1 mL of 200 mg Ca mL^{-1}, 5 mL of 20 mg Ba mL^{-1}, and 10 mL of 5 mg Fe mL^{-1} and stir.

3. With continuous mechanical stirring, add 6M NaOH until the solution is alkaline to Hydrion test paper. Then add about 60 mL of 2M Na_2CO_3 and stir.

4. Filter with suction through a double 15-cm glass fiber filter. Discard the precipitate, which should contain any alkaline earth metals, transition metals, rare earths, Sr, actinides, Ra, Pb, CrO_4^{-2}, PO_4^{-3}, and SO_4^{-2}.

5. To prepare the sample for ion exchange, titrate the filtrate to the orange-colored methyl red end point with 7.5M HNO_3.

6. Prepare an ion exchange column containing 10 mL of settled Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form). Wash the resin with 100 mL of 0.1M HNO_3.

7. Pass the solution from Step 5 through the resin bed at a full flow.

8. Wash with 500 mL of 0.1M HNO_3

9. Elute the Tc with 100 mL of 5M HNO_3.
10. Evaporate the eluate to dryness or near dryness, avoiding excessive heat.

ELECTRODEPOSITION

1. Add 1 mL of HCl to dissolve the residue. Transfer to an electroplating cell which contains a platinum disc, using three successive 1 mL water washes to complete the transfer.

2. Add one drop of 0.1% methyl red indicator. Add NH_4OH dropwise until the solution is yellow. Add the minimum amount of 1:5 HCl dropwise until the solution is red, then add two drops of 1:5 HCl in excess.

3. Dilute to 5 mL with water and connect to the electrodeposition apparatus. Electroplate onto the platinum disc cathode while stirring at a current of 1.2 A. The plating cell is supported on a lucite pedestal which is immersed in an ice water bath throughout the electrodeposition. (The platinum disc is flamed over a Bunsen burner before uranium is used to remove traces of oil and grease.)

4. Observe the voltage versus time curve. When the curve breaks (after about 1 h), quench the electrolyte with 1 mL of NH_4OH. Immediately turn off the current, dismantle the cell, and rinse the electroplated disc with water and ethanol. Dry on a hot plate with gentle heat.

5. Mount the plated platinum disc on a plastic disc. Centering is facilitated if the plastic discs are machined with an appropriate sized, shallow depression. Place a β scintillation phosphor directly over the platinum disc, cover with Mylar, and fasten with a nylon ring.

MEASUREMENTS

Count the platinum sample disc with a Ge(Li) γ-ray spectrometer, integrate the 204 keV line and record the date. Determine the spectrometer response at this energy for a 100% chemical yield with platinum discs onto which known quantities of ^{95m}Tc from the stock tracer solution have been electroplated. The ratio of these two activities, corrected to the same date, provides the chemical yield of the sample.

Count the platinum sample disc in a shielded low-level β scintillation counter and record the date. Calibrate the counting efficiency of this system for ^{99}Tc with platinum discs containing known quantities of ^{99}Tc. Also count the platinum discs electroplated with known quantities of ^{95m}Tc and record the date. The ^{99}Tc activity in the sample is determined by correcting for counter background and for the β contribution from the ^{95m}Tc tracer, and by adjusting for chemical yield and counting efficiency:

$$^{99}\text{Tc Bq} = \frac{(A - C)}{Y \times E}$$

where

A = net β cps of sample

C = β cps from ^{95m}Tc tracer

Y = chemical yield

E = counting efficiency

and

$$C = \gamma \bullet R$$

where

γ = net γ cps of sample from the Ge(Li) γ-ray spectrometer at 204 keV, decay corrected to the time of the sample β count.

R = mean ratio of the net β cps of the ^{95m}Tc standard discs to the net γ cps of these same discs from the Ge(Li) γ-ray spectrometer at 204 keV; both activities are decay corrected to the same time. For the EML systems, this ratio (R) is about 0.5.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	0.05
Yield	(%)	80
^{95m}Tc Interference*	(cps)	0.07
LLD (1000)	(mBq)	0.07
LLD (3000)	(mBq)	0.03
LLD (10,000)	(mBq)	0.02

* The ^{95m}Tc tracer interacts with the phosphor in the EML low-level β scintillation counters producing about 0.5 β counts sec^{-1} for each sec^{-1} registered in the 204 keV photopeak of our Ge counts (Li) γ-ray spectrometer. The ^{95m}Tc interference can be reduced by a factor of two if the sample is held 61 days before β counting.

Thorium

Environmental Measurements Laboratory
U.S. Department of Energy

Th-01-RC

THORIUM IN URINE

APPLICATION

This procedure was developed primarily for the estimation of Th in urine from medically and occupationally exposed persons (Fisenne et al., 1986).

Thorium is equilibrated with ^{234}Th tracer and collected from wet-ashed urine by coprecipitation with Ca as the acidic oxalate. The Th is then separated from Ca by coprecipitation with Fe hydroxide and purified from Ra and most other α emitters by anion exchange in an 8N HNO_3 medium. Finally, Th is electrodeposited on a platinum disc from a dilute HCl solution. (**Note:** The Th may be prepared for α spectrometry by the microprecipitation method, Procedure G-03, Vol. I). The ^{228}Th, ^{230}Th, and ^{232}Th contents are determined by α spectrometry after measuring the total Th recovery by ß counting the ^{234}Th tracer. Radium can be determined in the same sample.

SPECIAL APPARATUS

1. Ion exchange columns - see Specification 7.5, Vol. I.

2. Plating cells - see Specification 7.16, Vol. I.

SPECIAL REAGENTS

1. Thorium-234 tracer solution (see Appendix).

2. Bio-Rad AG 1-X4 (100-200 mesh) anion exchange resin - see Specification 7.6, Vol. I.

3. Oxalic wash solution - prepare a dilute oxalic solution so that the pH is 3.5.

SAMPLE PREPARATION

1. Add a weighed amount of ^{234}Th tracer (about 2000 ß cps) to the urine sample and reagent blanks.

2. Wet ash the urine with HNO_3 and evaporate to a small volume.

3. Add 500 mL of H_2O, 100 mg of additional Ca, and 1 g of oxalic acid. Stir with a magnetic stirrer.

4. Adjust the pH to about 3.5 with NH_4OH.

5. Cool and filter by gravity on a Whatman No. 42 filter paper. Wash the precipitate with oxalic acid wash solution. (**Note:** Save the filtrate and washings for Ra determination.)

6. Place the precipitate and filter paper in a 400 mL beaker and wet ash with HNO_3. Evaporate just to dryness.

7. Dissolve the residue with HNO_3, add 200 mL H_2O, and 10 mg of Fe carrier. Adjust the pH to 8 with NH_4OH.

8. Cool and filter by gravity on a Whatman No. 42 filter paper. Wash the precipitate with H_2O. (**Note:** Save the filtrate and washings for Ra determination. Combine with the filtrate from Step 5.)

9. Place the precipitate and filter paper in a 250-mL beaker and wet ash with HNO_3. Evaporate just to dryness.

10. Dissolve the residue with HNO_3 and transfer to a 90-mL centrifuge tube with H_2O. Adjust the pH to 8 with NH_4OH.

11. Centrifuge and add the supernate to the solutions reserved for Ra determination.

12. Dissolve the precipitate in the centrifuge tube with 40 mL of 8N HNO_3.

DETERMINATION

1. Prepare an ion exchange column (see Specification 7.5, Vol. I) with 15 mL of purified Bio-Rad AG 1-X4 (100-200 mesh) resin (see Specification 7.5, Vol. I). Condition with 200 mL of 8N HNO_3. Check the column effluent with $AgNO_3$ to insure that the column is Cl^- free.

2. Pass the sample from **Sample Preparation**, Step 12, through the column at a flow rate of 1 mL min^{-1}.

3. Wash the column with 200 mL of 8N HNO_3. (**Note:** Combine the effluent and wash solutions with the solutions reserved for Ra determination. This combined solution may be used for the determination of Ra by coprecipitation with Ba as the SO_4^{-2} and measurement by Rn emanation.)

4. Elute the Th into a 250 mL beaker with 200 mL of 1N HNO_3. Discard the resin.

5. Evaporate the solution to dryness, wet ash the residue with HNO_3 and evaporate to dryness again.

6. See Electrodeposition of the Actinides: Talvite Method, G-02, Vol. I.

7. Measure the ^{234}Th activity by ß counting to determine the Th recovery.

8. Measure the ^{232}Th, ^{230}Th, and ^{228}Th by α spectrometry and correct for ^{234}Th recovery.

LOWER LIMIT OF DETECTION (LLD)

		^{230}Th, ^{232}Th	^{228}Th
Counter Efficiency	(%)	40	40
Counter Background	(cps)	1.7×10^{-5}	8.3×10^{-5}
Yield	(%)	70	70
Blank	(cps)	-	-
LLD (400 min)	(mBq)	0.44	1.0
LLD (1000 min)	(mBq)	0.28	0.62

* Reagent blanks must be analyzed with the samples.

APPENDIX

PREPARATION OF ^{234}Th TRACER SOLUTION

A. Column preparation.

Prepare three anion exchange columns (see Specification 7.5, Vol. I) with 25 mL of Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form) resin (see Specification 7.4, Vol. I). Convert the resin to the proper form by washing with 10 column volumes (250 mL) of 7N HCl.

B. Initial separation.

1. Weigh 5 g of U_3O_8 into a 250-mL beaker and dissolve in HCl.

2. Dilute the solution with 100 mL of 7N HCl.

3. Transfer the solution to the ion exchange column, police, and wash the beaker with 7N HCl. Transfer the washings to the column.

4. Wash the column with 250 mL of 7N HCl.

5. Discard the effluent and washings containing ^{234}Th and ^{230}Th.

6. Strip the U from the column with 250 mL of 1N HCl into a 400-mL beaker. Evaporate the solution to dryness.

7. Allow the ^{234}Th (24.1 day) to build up for 24 h. (**Note:** Allowing a 24 h build-up period produces about 1500 Bq of ^{234}Th and only 0.17 Bq of ^{230}Th.)

C. Final tracer preparation.

1. Dissolve the previously separated U salt in 100 mL of 7N HCl.

2. Transfer the solution to a 7N HCl anion exchange column, police, and wash the beaker with 7N HCl. Transfer the washings to the column.

3. Allow the solution to drain into a 250-mL beaker.

4. Transfer the effluent to a second ion exchange column. Collect the effluent containing the ^{234}Th in a 400-mL beaker.

5. Wash the second column with 50 mL of 7N HCl. Combine with the effluent in the 400-mL beaker.

6. Strip the U from the two columns with 250 mL of 1N HCl. Combine the solutions, evaporate to dryness, and retain the salt for future additional tracer production. Discard the resin.

7. Evaporate the ^{234}Th solution to near dryness, wet ash with HNO_3, and make up to 50 mL of 1N HNO_3. Store the ^{234}Th tracer solution in a polyethylene bottle.

8. Weigh an aliquot of ^{234}Th tracer solution onto a platinum disc, dry, flame, and beta count.

Note:

For sequential U-Th analyses, the ^{234}Th tracer solution must be checked either by fluorimetry or α spectrometry for possible U contamination.

Uranium

Environmental Measurements Laboratory
U.S. Department of Energy

U-01-RC

ENRICHED URANIUM IN URINE

APPLICATION

The procedure described is capable of handling up to 1 L of urine or water (Hindman, 1983; Sill and Williams, 1981; Welford et al., 1960).

Uranium is collected by alkaline phosphate precipitation and is isolated from urine constituents by ion exchange. The uranium is microprecipitated for α-spectrometry measurement. Uranium-232 tracer is used to determine the chemical recovery.

SPECIAL APPARATUS

1. Ion exchange columns - see Specification 7.5, Vol. I.

2. Mercury cathode apparatus, Eberbach Dyna-Cath or similar.

3. Polyethylene dispensing bottles - see Specification 7.11, Vol. I.

4. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03, Vol. I.

SPECIAL REAGENTS

1. Bio-Rad AG 1-X4 (100-200 mesh), anion exchange resin - see Specification 7.4, Vol. I.

2. Uranium-232 tracer solution - about 0.17 Bq g^{-1} of solution in a dispensing bottle.

3. Mercury - triply distilled.

SAMPLE PREPARATION

1. Add 20 mL of 1:9 phosphoric acid and 150 mL of HNO_3 to 1 L of a 24 h urine specimen in a 1500-mL beaker. Add a known aliquot, about 0.1 g of ^{232}U tracer solution (see **Note 1**).

2. Cover and boil gently for 1 h. Allow to cool slightly and add NH_4OH to precipitate the alkaline earth phosphates (~ pH of 9). Add 10 mL of NH_4OH in excess.

3. Digest on a steam bath with occasional stirring for 1 h.

4. Filter by gravity on a 15 cm Whatman No. 41 filter paper and discard the filtrate.

5. Wash the original beaker with four 25-mL portions of 1:1 HNO_3, pouring the acid through the paper each time to dissolve the precipitate. Collect the solution in a 250 mL beaker. Discard the filter paper.

6. Wet ash the residue to a white salt by the addition of small amounts of HNO_3 and evaporate to near dryness on a medium hotplate.

7. Convert the solution to the Cl^- form with two successive 5-mL portions of HCl. Evaporate the solution to dryness on a medium hotplate.

8. Dissolve the residue in a minimum of 7N HCl ($\leq$50 mL), with heating and stirring. Cool the solution to room temperature.

DETERMINATION

1. Pass the solution through a prepared resin column (see **Note 2**) at a flow rate of <2 mL min^{-1}. Discard the effluent.

2. Wash the column with 400 mL of 7N HCl at a flow rate of 2 mL min^{-1}.

3. Elute the U from the resin with 200 mL of 1N HCl, collecting the eluate in a 250-mL beaker. Discard the resin.

4. Evaporate the eluate to near dryness.

Notes:

1. It is necessary to analyze reagent blanks with each batch of samples to correct the U results.

2. Transfer 10 mL of the wet resin to the ion exchange column, pass 7N HCl through the column until the effluent is 7N. About 200 mL of 7N HCl is necessary. Use fresh resin for each sample.

GENERIC MERCURY CATHODE ELECTROLYSIS SEPARATION

Note:

Removal of iron is not required when the microprecipitation source preparation is performed, see Procedure G-03, Vol. I.

1. Destroy any residual organic material with dropwise additions of HNO_3.

2. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl. Cool the beaker and add 75 mL of 2:98 H_2SO_4. Warm the beaker gently to dissolve any residue and cool to room temperature.

3. Add 20 mL of Hg to the beaker. Electrolyze the solution with the Hg cathode unit for 1 h at 5 A. Remove the electrodes and rinse with H_2O.

4. Gravity filter the sample through a 15 cm Whatman No. 41 paper into a 250-mL beaker. Wash the filter and Hg with hot water. Reserve the Hg for cleaning and reuse. Discard the filter.

5. Evaporate the filtrate to SO_3 fumes. Destroy any organic matter with dropwise additions of HNO_3.

6. Convert the sample to the Cl^- form with three successive additions of 5 mL of HCl. Evaporate the solution to dryness.

7. Follow Microprecipitation of the Actinides, Procedure G-01. **Note:**The sample may be prepared for α spectrometry using Electrodeposition of the Actinides, Talvitie Method, Procedure G-02, Vol. I.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33×10^{-6} for ^{238}U 3.33×10^{-6} for ^{235}U 6.67×10^{-6} for ^{234}U
Yield	(%)	75
Blank	(cps)	5.00×10^{-5} for ^{238}U 5.00×10^{-5} for ^{235}U 1.00×10^{-3} for ^{234}U
LLD (400 min)	(Bq)	6.7×10^{-4} for ^{238}U 6.7×10^{-4} for ^{235}U 3.2×10^{-3} for ^{234}U
LLD (1000 min)	(Bq)	4.7×10^{-4} for ^{238}U 4.7×10^{-4} for ^{235}U 2.0×10^{-3} for ^{234}U
LLD (5000 min)	(Bq)	2.0×10^{-4} for ^{238}U 2.0×10^{-4} for ^{235}U 8.3×10^{-4} for ^{234}U

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Anal Chem, 53, 412-415 (1981)

Welford, G. A., R. S. Morse and J. S. Alercio
"Urinary Uranium Levels in Non-Exposed Individuals"
Am. Ind. Hyg. Asso. J., 21 (1960)

U-04-RC

URANIUM IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS

APPLICATION

This procedure has been used to analyze bone, soil, food, tissue, air filters, and water samples (Welford et al., 1960).

Uranium is leached from the dry-ashed residue, isolated by anion exchange chromatography plus Hg cathode electrolysis and is determined by its fluorescence when fused with NaF and exposed to ultraviolet light.

SPECIAL APPARATUS

See Uranium in Urine - Fluorimetry (Procedure U-01-E).

In addition:

1. Ion exchange columns - see Specification 7.5, Vol. I.

2. Mercury cathode electrolysis unit (Eberbach Dyna-Cath or similar).

3. Polyethylene dispensing bottle - see Specification 7.11, Vol. I.

SPECIAL REAGENTS

See Uranium in Urine - Fluorimetry (Procedure U-01-E).

In addition:

1. Bio-Rad AG 1-X4 (100-200 mesh) anion exchange resin - see Specification 7.4, Vol. I.
2. ^{232}U tracer solution ~ 40 Bq g^{-1} of solution in a dispensing bottle.
3. Mercury - triply distilled.

SAMPLE PREPARATION

A. Bone and tissue.

1. Dry ash the sample according to the procedure used for ^{90}Sr (see Sr-02-RC).
2. Weigh out 10 g of ash into a 400-mL beaker. Add a weighed aliquot (~ 0.1 g) of ^{232}U tracer solution (see **Note 1**).
3. Add 200 mL of HNO_3 to the beaker and evaporate slowly to dryness.
4. Repeat acid addition and evaporation with 25-mL portions of HNO_3 until a white residue is obtained (see **Note 2**).
5. Add 25 mL of HCl. Evaporate to dryness and repeat the HCl addition and evaporation twice more.
6. Dissolve the residue in a minimum ($\leq$ 50 mL) of 7N HCl.
7. Continue with **Separation**.

B. Food and soil.

1. Weigh 10 g of food ash or soil into a 100-mL platinum dish and add a weighed amount (~ 0.1 g) of ^{232}U tracer solution (see **Note 1**).

2. Dry on a hot plate and fuse with four times the sample weight of Na_2CO_3 in an electric muffle furnace at 900°C.

3. Cool and transfer the melt to a 400-mL beaker. Place a magnetic stirring bar in the beaker.

4. Wash the platinum dish with 25 mL of HNO_3. Add the washings slowly to the beaker. Add an additional 75 mL of HNO_3 to the beaker. Cover the beaker and place on a pyromagnetic stirrer unit.

5. Add 100 mL of $HClO_4$ to the beaker and heat while stirring until perchloric acid fumes are evolved.

6. Remove the beaker from the stirrer unit. Cool, add 100 mL of HNO_3 and heat with stirring until the total volume is reduced to ~ 75 mL.

7. Cool the beaker and add 150 mL of H_2O. Filter by gravity through a Whatman No. 42 filter paper.

8. Wash the precipitate with 100 mL of hot 1:10 HNO_3 followed by an equal volume of hot water. Discard the residue.

9. Evaporate the filtrate slowly to dryness. Repeat the acid treatment and evaporation if necessary to obtain a white residue.

10. Add 25 mL of HCl. Evaporate to dryness and repeat the HCl addition and the evaporation twice more.

11. Dissolve the residue in a minimum ($\leq$ 50 mL) of 7N HCl.

12. Continue with **Separation**.

C. Water.

1. Evaporate the total H_2O sample to a small volume.

2. Add a weighted quantity of ^{232}U tracer solution (~ 0.1 g) and evaporate to dryness. Dissolve the residue in 100 mL of HNO_3 (see **Note 1**).

3. Evaporate several times with additions of 25-mL portions of HNO_3 (see **Note 2**).

4. Dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.

5. Dissolve the residue in a minimum ($\leq$ 50 mL) of 7N HCl and continue with **Separation**.

D. Air filters.

1. Add a weighted aliquot (~ 0.1 g) of ^{232}U tracer directly to the filter in a platinum dish and dry ash in an electric muffle at 550°C overnight (see **Note 1**).

2. Dissolve the residue in HNO_3 and transfer the solution to a 250-mL beaker.

3. Evaporate to dryness several times with 25-mL additions of HNO_3 (see **Note 2**).

4. Add 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.

5. Dissolve the residue in a minimum ($\leq$ 50 mL) of 7N HCl.

6. Continue with **Separation**.

SEPARATION

1. Pass the 7N HCl sample solution obtained during sample preparation through a prepared anion exchange column (see **Note 3**).

2. Wash the column with 400 mL of 7N HCl.

3. Elute with 200 mL of 1N HCl and collect the eluate in a 250-mL beaker. Evaporate the solution to dryness.

4. Perform **Generic Mercury Cathode Electrolysis Separation** (see Procedure U-01-E).

5. Evaporate the filtrate to dryness. Add 5 mL HNO_3 and evaporate to dryness.

6. Dissolve the residue in 2-3 mL of HNO_3. Cool, transfer to a 10 mL volumetric flask, and dilute to the mark with H_2O.

7. Deposit 0.1 mL on a stainless steel disk, dry, and α count for recovery of ^{232}U. Correct the fluorimetric readings by this recovery factor.

8. Measure the U fluorimetrically as described in Procedure U-01-E.

Notes:

1. It is necessary to analyze reagent blanks with each batch of samples to correct the U results.

2. If silicious material is present, transfer the sample to a 100-mL platinum dish or a 100-mL Teflon beaker with HNO_3. Add 10 mL of HF to the vessel and evaporate to dryness. Repeat additions of 25 mL HNO_3 and 10 mL of HF as necessary to volatilize the silica. Remove the HF by adding three successive 10-mL volumes of HNO_3 to the vessel and evaporating to dryness.

3. 10 mL of Bio-Rad AG 1-X4 is used, prepared according to Specification 7.4, Vol. I, and conditioned with 200 mL of 7N HCl.

DETERMINATION

See Uranium in Urine - Fluorimetry (Procedure U-01-E).

REFERENCE

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